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1952, No. 3

May-June

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ELECTROCHEMICAL BEHAVIOR OF IRON IN OXIDIZING MEDIA

COMMUNICATION 3. CATHODIC POLARIZATION OF IRON IN OXIDIZING MEDIA

L. Ya. Gurvich and G. V. Akimov*

The cathodic polarization of iron has been the object of a number of investigations. In a study of the cathodic polarization of iron in a buffered solution in an atmosphere of air and oxygen, Tomashov [1] found that the value of the limiting diffusion current was proportional to the partial pressure of oxygen. In an investigation of the cathodic polarization of copper in H_2O_2 solutions of varying concentration, Tomashov again found a linear relationship between the limiting diffusion current and the H_2O_2 concentration. Glasstone and Hickling [2] point out that the limiting current is proportional to the concentration of depolarizer when the processes are reversible, but for irreversible processes it is proportional to c^n, where c is the concentration of depolarizer and n has a value between 0.6 and 1.

Krasilshchikov [3] has carried out an investigation of the cathodic behavior of iron in a number of solutions, including oxidizing media: KNO_3 and $K_2Cr_2O_7$ solutions. He found that increase in concentration of KNO_3 from 0.1 N to 1.0 N causes a displacement of the curves in the region of the ionization of oxygen in the direction of more positive values; in the region of hydrogen evolution, the curves for 0.1 N and 1.0 N are practically coincident. We have carried out an investigation of cathodic polarization in solutions of KNO_3 and HNO_3 in the concentration range 0.0001 N–0.1 N and in 0.1 N solutions of $K_2Cr_2O_7$, $KMnO_4$, and $(NH_4)_2S_2O_8$ (see Table).

The preparation of the electrodes consisted in polishing on abrasive cloth — successively from coarse to finer grades (6/0) — washing with water, and degreasing with alcohol. The electrodes were cylindrical, having a base diameter of 55 mm, and they were cemented into glass jackets by means of Bakelite, as described in Tomashov's book. The potentials were measured on a potentiometer with the aid of a calomel electrode (saturated KCl). The arrangement was shown diagrammatically in our previous communication (4).

In our investigation of the cathodic behavior of iron in 0.1 N and 1.0 N KNO_3 solutions, we have not found the concentration of this oxidizing agent to have an appreciable effect. As Fig. 1 shows, the return branches of the cathodic polarization curves are almost straight lines for high current density in the region of the hydrogen overvoltage. On the return branches, there are no inflections characteristic of the diffusion region. When the current has been cut off, the potential is found to be greatly displaced towards the negative side. The cathodic current evidently removes an oxide or adsorbed film, which, on reduction of the current density (partially, or even to zero), is not reformed in the solution under investigation during the time of measurement.

A cathodic curve determined when the solution is being stirred passes lower than the curve for the still solution. The diffusion region is then moved in the direction of greater current densities. The region of hydrogen evolution on the curve for a moving liquid begins at higher current densities than on the curve for the still solution. The return branch of the curve is displaced with respect to the outward branch in the diffusion and oxygen-ionization regions in the direction of more positive potentials; this was observed also by Tomashov for the cathodic curves given by the solutions investigated by him. The final potential obtained after cutting off the current is more negative than the original potential. The difference between the initial and final potentials in a moving electrolyte is much less than in a still one (in the first case 300 mv, in the second case less than 100 mv). It is evident that

* With participation of T. M. Samet.

TABLE

Cathodic Polarization of Iron in Various Media (electrode potential values are given in mV on the hydrogen scale)

Solution	Current density (amp/sq.cm)									
	without current		$2 \cdot 10^{-3}$		$5 \cdot 10^{-3}$		$1 \cdot 10^{-2}$		$1 \cdot 10^{-1}$	
	initial	final	outward path	return path	outward path	return path	outward path	return path	outward path	return path
0.1 N KNO_3	−145	−570	−310	−645	−540	−690	−715	−725	−845	−720
0.1 N KNO_3 with stirring	−25	−118	−135	−100	−175	−155	−220	−210	−465	−450
1 N KNO_3	−170	−643	−320	−890	−450	−720	−600	−725	−760	−780
			−260		−615		−720		−810	
0.0001 N HNO_3	−190	−438	−435	−640	−600	−675	−715	−715	−800	−710
0.001 N HNO_3	−375	−600	−400	−645	−560	−690	−725	−720	−830	−830
0.01 N HNO_3	−332	−771	−330	−580	−385	−645	−385	−735	−705	−810
0.05 N HNO_3	−302	−307	−310	−295	−310	−295	−315	−295	−365	−315
0.1 N HNO_3	−230	−292	−225	−265	−230	−270	−235	−265	−255	−275
0.1 N KNO_3 0.01 N $Fe(NO_3)_3$	−370	−668	−400	−710	−620	−740	−725	−765	−875	−875
0.1 N $K_2Cr_2O_7$	+200	+137	−335	−385	−550	−515	−625	−575	−960	−900
0.1 N $KMnO_4$	+615	+565	+560	+540	+520	+190	+380	+460	+250	+250
0.1 N $(NH_4)_2S_2O_8$	−287	−300	−300	−300	−300	−300	−300	−300	−300	−300
0.1 N $(NH_4)_2S_2O_3$ 0.1 N NH_4OH	−331	−234	−330	−340	−330	−345	−325	−350	−605	−565

stirring makes it possible for the film to be regenerated, owing to the intensified supply of oxidant.

At the beginning of the region of hydrogen evolution, at a current density of $1 \cdot 10^{-3}$ amp/sq.cm, the electrode potential is −775 mV. The equilibrium hydrogen potential in neutral solution has the value −414 mV. The overvoltage of hydrogen is therefore 361 mV. At this current density, Frumkin found a value of 0.35 V for the overvoltage of hydrogen at iron [1].

In order to elucidate the part played by depolarization with participation of NO_3' ions, we determined the cathodic curve for iron in 0.01 N HNO_3, with an addition of urea (2 g per liter of solution) (Fig.2). Addition of urea must slow down the depolarization process, which corresponds to the reaction $NO_3' + e = NO_2'$, for urea destroys the NO_3' ions, which act catalytically on this process. As Fig.2 shows, urea has no appreciable influence on the cathodic curve for iron in 0.01 N HNO_3, and consequently, depolarization by NO_3' ions does not play any significant part.

The introduction of KNO_3 into 0.01 N HNO_3 (0.75 g per liter of solution) does not permit the depolarizing role of the ions $+ NO_2'$ to be ascertained, for the effect of the NO_3' ions goes beyond the limits of catalytic acceleration of depolarization by the aid of NO_2' ions. KNO_3 acts as a depolarizer on its own account, and it greatly displaces the initial electrode potential of iron to the positive side and changes the course of the cathodic curve.

In order to ascertain the effect of iron ions formed in the corrosion process, the cathodic curve of iron was determined in 0.1 N KNO_3 with the addition of 0.01 g-equiv of $Fe(NO_3)_3$ per liter of solution. It was found (Fig.1) that, while displacing the initial potential of the iron in the negative direction, the Fe^{3+} ions did not alter the essential picture of the cathodic polarization of iron. The hydrogen overvoltage in a solution containing Fe^{3+} is somewhat higher than in pure 0.1 N KNO_3 (by approximately 50 mV). After the experiment, flocs of $Fe(OH)_3$ were to be found in the cathode space. This may have been due to evolution of hydrogen at the cathode with a corresponding increase in the concentration of OH' until the solubility product of $Fe(OH)_3$ was reached. It is possible also that the precipitation of $Fe(OH)_3$ was due to coagulation of its colloidal solution at the cathode.

1·10⁻⁴ outward path	1·10⁻⁴ return path	Current density at which gas evolution begins	Appearance of Electrode after Test
−930	−930	$1.04 \cdot 10^{-3}$	Electrode surface glistening; thin yellow spots at edges.
			Yellow spots in places on glistening electrode surface.
−840	−840		No change.
		$1.3 \cdot 10^{-4}$	Surface of electrode light-colored and glistening.
		$1.7 \cdot 10^{-3}$	Electrode surface gray; dark spots in places.
−980	−960	$1.1 \cdot 10^{-2}$	Darkening of electrode surface; insignificant pitting.
−950	−900	$9.6 \cdot 10^{-3}$	Uneven layer of black and yellow corrosion products on the electrode surface. Electrolyte had become deep yellow.
−335	−335	$7.1 \cdot 10^{-4}$	A black readily removable film on the electrode; the surface under this corroded; electrolyte greenish yellow.
−920	−930	$1.3 \cdot 10^{-2}$	Electrode unchanged; precipitate in electrolyte.
		$4.02 \cdot 10^{-4}$	No change.
			Electrode covered with a fine crystalline black powder.
−720	−720	$1.7 \cdot 10^{-3}$	Dark gray corrosion products firmly fixed to the electrode surface.
−800	−800		Black readily removable film on the electrode; the surface under this corroded.

This colloidal solution is formed by the hydrolysis of $Fe(NO_3)_3$ and contains positive micelles $Fe(OH)_3Fe^{3+}$, which can be discharged at the cathode.

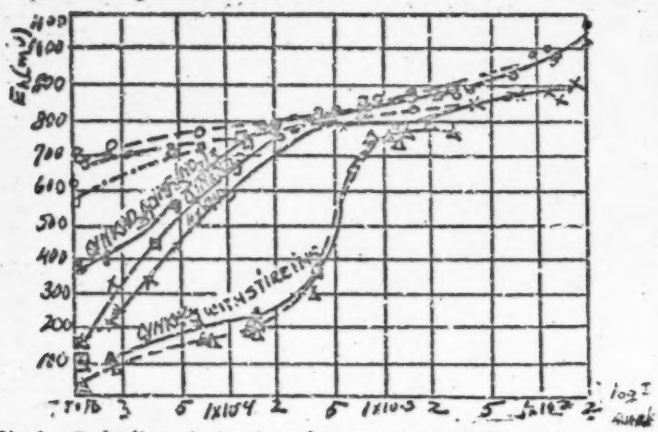

Fig.1. Cathodic polarization of iron in 0.1 N KNO_3: with stirring (▲ — outward path, △ — return path); in a still solution (■ — outward path, □ — return path); and in a still solution with addition of $Fe(NO_3)_3$ (● — outward path, ○ — return path)

The absence that we have found of any great effect due to iron ions on the cathodic polarization of iron in 0.1 N KNO_3 is in sharp contrast with the effect of Fe^{3+} ions, as observed by Tomashov [1] in the solution 0.5 N NaCl + 0.005 N Na_2CO_3 + 0.005 N $NaHCO_3$. The cathodic curve for iron, investigated by Tomashov in this solution with additions of $FeCl_3$, reveals an almost complete absence of polarization, resulting from depolarization according to the reaction: $Fe^{3+} + e \longrightarrow Fe^{2+}$; as the concentration of this depolarizer (Fe^{3+}) is high in comparison with the concentration of oxygen (0.001 N), depolarization proceeds mainly on account of ferric ions, with corresponding acceleration of the corrosion process. Consequently, in the case studied by Tomashov, the acceleration of corrosion on account of ferric ions has a cathodic mechanism. In our case, the observed acceleration of corrosion under the action of ferric ions is connected not with a cathodic, but with an anodic process, as shown in our previous communication [4].

Results of investigations on the effect of the HNO_3 concentration on the cathodic polarization of iron are presented in Fig.3. In all experiments, the NO_3' concentration was maintained constant at 0.1 N. Solutions having various pH values were prepared by dissolving the corresponding amounts of acid in 0.1 N KNO_3.

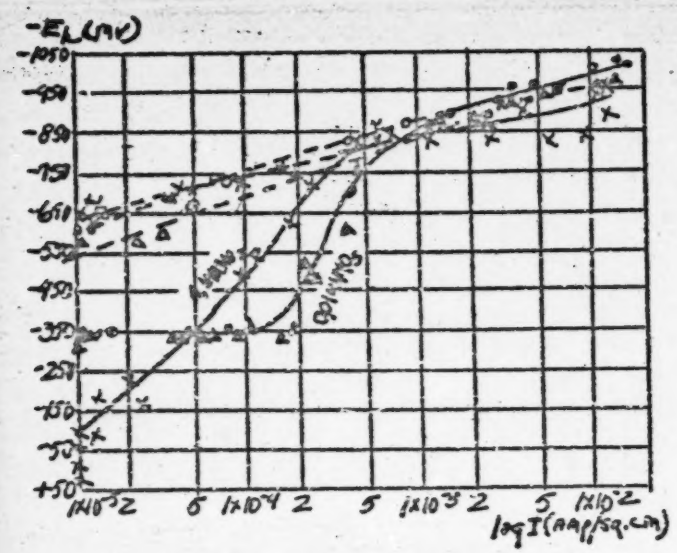

Fig.2. Cathodic polarization of iron: in 0.1 N KNO_3 (× — outward path, x — return path); in 0.01 N HNO_3 (● — outward path, ○ — return path); in 0.01 N HNO_3 with addition of urea (▲ — outward path, △ — return path)

A number of interesting relations can be established from the cathodic curves. Increase in the concentration of acid displaces the diffusion threshold in the direction of higher current density. In 0.05 N HNO_3, the polarization was found to be unstable. The return branch of the curve for 0.05 N HNO_3, in contrast with curves for weaker solutions, does not keep to negative values of the potential. In 0.1 N HNO_3, no appreciable polarization is to be observed; at the current densities with which we worked (up to $2 \cdot 10^{-2}$ amp./sq.cm), we did not attain the diffusion threhold. A similar effect of pH on the displacement of the diffusion current was observed by Krasilshchikov [3] when studying the behavior of iron in solutions of sulfuric acid.

The regions of hydrogen evolution for different HNO_3 concentrations do not vary greatly. The return branches of the cathodic curves for solutions of low concentration, right up to 0.01 N HNO_3, do not differ greatly from one another, and in the region of oxygen ionization they pass on the negative side of the outward branches. It is evident that in weakly acid solutions (up to 0.1 N), on switching off the current, the potential is greatly displaced in the negative direction from its original value, because the oxide film is not reformed in these solutions. In 0.05 N HNO_3, the oxide film is reformed when the current density is diminished, and in 0.1 N HNO_3 the film is not removed, even at very high current densities, owing to the powerful oxidizing action of the solution.

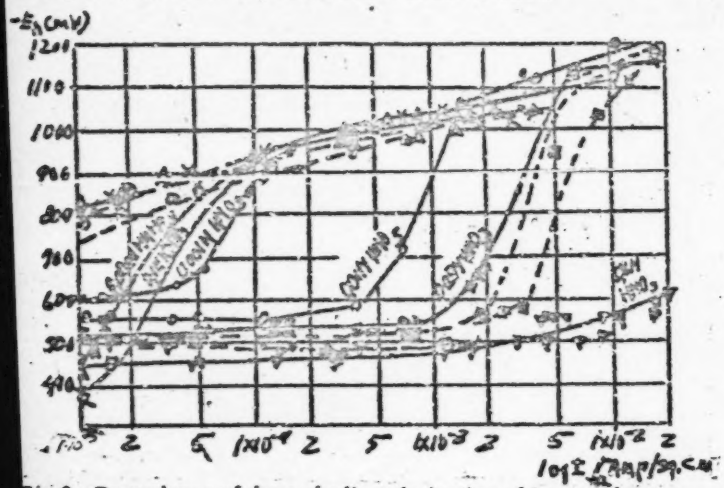

Fig.3. Dependence of the cathodic polarization of iron on the concentration of nitric acid.

We have studied the cathodic polarization of iron also in 0.1 N solutions of $KMnO_4$, $K_2Cr_2O_7$, and $(NH_4)_2S_2O_8$ (Fig.4). The electrode potential of iron is most positive in a solution of potassium permanganate. When working with current densities of the order 10^{-3} amp./sq.cm, we did not attain the diffusion threhold in this solution; the polarization of iron in a $KMnO_4$ solution is not great. After the trials, a compact black film was found on the electrodes, and, on removing it, we obtained fine crystalline MnO_2 powder. The action of $KMnO_4$ as a depolarizer proceeds according to the equation 2; the equilibrium potential of this process is 1.128 V.

iron is very highly polarized in a $K_2Cr_2O_7$ solution, and the return and outward branches of the cathodic curve do not coincide; the final potential is about 300 mV more negative than the initial potential. In the region of hydrogen overvoltage, the curve for 0.1 N $K_2Cr_2O_7$ is disposed rather more in the negative direction than the curve for 0.1 N KNO_3; thus, the potential of iron at a current density of $1 \cdot 10^{-3}$ amp/sq.cm is respectively −950 mV and −775 mV for these two solutions.

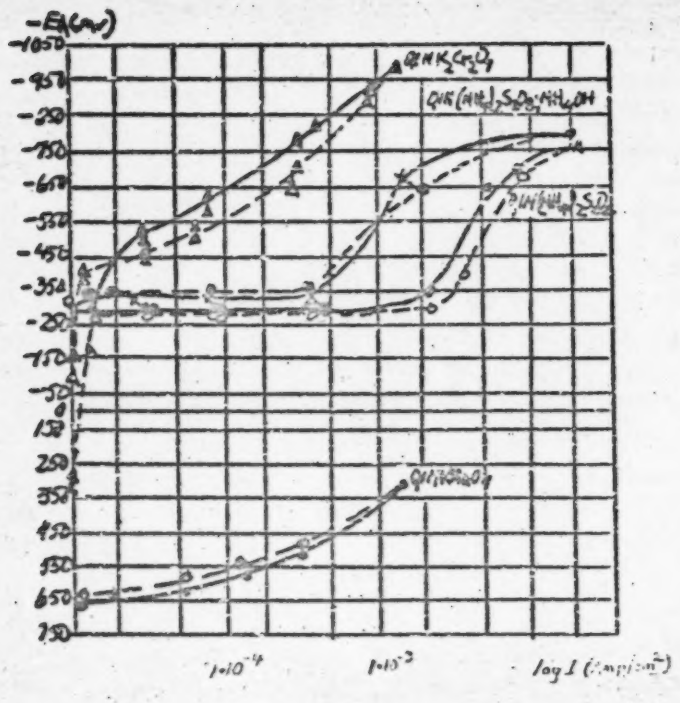

Fig.4. Cathodic polarization of iron in 0.1 N solutions of: $KMnO_4$ (O — outward path, ● — return path); $K_2Cr_2O_7$ (▲ — outward path, △ — return path); $(NH_4)_2S_2O_8$ (■ — outward path, □ — return path); $(NH_4)_2S_2O_8$ with addition of NH_4OH (× — outward path, ● — return path)

As was shown in the previous communication [4], the electrode potential of iron in a solution of $(NH_4)_2S_2O_8$, a powerful oxidant, has a fairly high negative value (about −275 mV). The peculiarity of the cathodic curve of iron in this oxidant is the non-polarizability of the electrode up to high values of current density ($1.9 \cdot 10^{-3}$ amp/sq.cm); the region of hydrogen evolution also is displaced to higher current densities, in comparison with the curves for nitrate solutions. The initial and final potentials of iron after cathodic polarization in $(NH_4)_2S_2O_8$ solution are coincident.

Feebie gas evolution is to be observed already at a current density of $1.37 \cdot 10^{-5}$ amp/sq.cm, and it becomes more intense at $5.61 \cdot 10^{-5}$ amp/sq.cm, which corresponds to the beginning of hydrogen evolution. At a current density of $3.43 \cdot 10^{-5}$ amp/sq.cm, formation of an $Fe(OH)_3$ precipitate is to be observed. It is evident that, owing to fairly intense corrosion, the concentration of Fe^{3+} in the $(NH_4)_2S_2O_8$ solution is so high that separation of hydrogen at the cathode leads to increase in the OH' concentration at the cathode surface until the solubility product of $Fe(OH)_3$ is attained.

At high current densities ($1.94 \cdot 10^{-2}$ amp/sq.cm) a cloudiness appears in the cathode liquid, caused evidently, by the separation of sulfur in the colloidal condition from the ammonium persulfate. We determined the cathode curve of iron in 0.1 N $(NH_4)_2S_2O_8$ with an addition of NH_4OH (0.1 g-equiv. per liter of solution). In an alkaline medium, the initial potential was somewhat displaced in the negative direction (about 40 mV), and the electrode remained unpolarized up to a current density of $3.4 \cdot 10^{-6}$ amp/sq.cm, i.e., in this case polarization sets in earlier than in neutral solution. The region of hydrogen evolution begins at a lower current density than for the solution without the NH_4OH addition. Flocs of $Fe(OH)_3$ make their appearance in the cathode space at a lower current density than that at which they appear in a neutral medium; they appear at $1.3 \cdot 10^{-5}$ amp/sq.cm.

SUMMARY

1. An investigation has been made of the cathodic polarization of iron in nitrate solutions containing nitric acid in varying concentration, the concentration of NO_3' ions being maintained constant. It has been shown that increase in the concentration of acid displaces the diffusion threshold in the direction of higher current density. In 0.1 N HNO_3 the diffusion threshold was not attained for current densities up to $2 \cdot 10^{-2}$ amp/sq.cm.

In neutral and weakly acid solutions (up to 0.01 N HNO_3), the potential of the iron after the current has been switched off has a greater negative value than the initial potential. For 0.05 N HNO_3, the hysteresis of the

cathodic curve is inappreciable because the oxidizing properties of the solution cause an oxide film to be formed rapidly; in the diffusion region, the return curve passes somewhat below the outward curve.

2. The effect of the concentration of KNO_3 on the cathodic polarization of iron has been investigated. It has been found that there is no essential difference between the courses of the cathodic curves in 0.1 N and 1.0 N solutions of KNO_3. It is evident that the main depolarizer in neutral and weakly acid solutions of nitrates is dissolved oxygen, and not NO_3' ions.

3. The effect of ferric ions on the cathodic polarization of iron in 0.1 N KNO_3 has been investigated. It has been found that ferric ions, while displacing the initial electrode potential in the negative direction, produce little change in the further course of the cathodic curve.

4. The effect of urea on the cathodic polarization of iron in an acid nitrate solution has been investigated. In this case, displacement of the diffusion threshold in the direction of lower current density is found. The cathodic polarization of iron in a solution containing KNO_3 (0.1 N) and HNO_3 (0.01 N) was investigated. It was found that in this case the effect of NO_2' ions cannot be explained by their catalytic effect on depolarization by the aid of NO_3' ions. KNO_2 acts as a depolarizer on its own account, and it greatly displaces the initial electrode potential of iron in the positive direction and changes the course of the cathodic curve.

5. The cathodic polarization of iron in 0.1 N solutions of $KMnO_4$, $K_2Cr_2O_7$, and $(NH_4)_2S_2O_8$ has been investigated. It has been found that in $K_2Cr_2O_7$ solution the iron electrode is strongly polarized and, in the hydrogen region, has a higher negative potential than that given in a KNO_3 solution at the same current density.

In a $KMnO_4$ solution over the range of current density studied (up to $6 \cdot 10^{-3}$ amp/sq.cm), the iron electrode is only weakly polarized. In an $(NH_4)_2S_2O_8$ solution, the electrode remains unpolarized up to a current density of $7 \cdot 10^{-3}$ amp/sq.cm; addition of NH_4OH reduces the diffusion threshold in an ammonium persulfate solution to the current density of $5 \cdot 10^{-4}$ amp/sq.cm.

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MECHANICAL PROPERTIES OF ALLOYS OF THE MAGNESIUM – CADMIUM SYSTEM

E. M. Savitsky and V. V. Baron

The phase diagram for alloys of the magnesium-cadmium system has been studied by many of our own scientists. One of the first was Academician Urazov [1]. This system was investigated by Stepanov and Bulakh [2,3], Komilov [4,5,6], Ageev and Ageeva [7], Rovinsky and Kozhina [8], Khomyakov, Kholler, and Torshkina [9], and Grum-Grzhimaylo [10]. The system magnesium-cadmium has been studied also by a number of foreign investigators [11,12,13,14,15,16].

As a result, the presence of three compounds: Mg_3Cd, MgCd and $MgCd_3$ has been established in this system. In spite of the large number of investigations, there are a number of obscurities in the structure of the diagram. Some authors consider that, when alloys of the magnesium-cadmium system are crystallized out, the compound MgCd is formed from the melt, and two other compounds, Mg_3Cd and $MgCd_3$, make their appearance in the solid state, when the temperature is lowered, as a result of a disorder→order process.

These authors assert that MgCd undergoes polymorphous change at about 250°. Other authors find that the melts in this system yield only solid solutions, from which, as the temperature is lowered, all three compounds separate as a result of the disorder→order process. According to the results of these investigations, the temperatures of formation of the compounds Mg_3Cd, MgCd, and $MgCd_3$ are 150, 250, and 89° respectively. In the solution of these questions, use may be made of a study of the mechanical properties of the alloys. However, as far as we are aware, the mechanical properties of alloys of the magnesium-cadmium system, apart from hardness determinations at room temperature, have hitherto remained without study. The measurements referred to were carried out only on cast specimens, whereas it is well known that the equilibrium state of alloys is attained appreciably more rapidly and completely when deformed specimens are used [17].

EXPERIMENTAL

In the present work we determined the hardness, tensile strength, plasticity under dynamic and static conditions, and the efflux pressure for cast and deformed alloys of this system in the quenched and annealed conditions at ordinary and at raised temperatures. The alloys were prepared from magnesium of 99.9% purity, mark MG1, and cadmium of 99.8% purity, mark KD 2.

Fusion was carried out under a carnallite flux, and, to prevent burning of the magnesium, the latter was introduced under a layer of melted cadmium. The compositions of the cast alloys are given in the Table.

Hardness measurements were made on cast specimens, 23 mm in diameter and about 50 mm long, at room temperature. The hardness of the alloys was determined with the aid of a Fobedite cone and was calculated from the formula

$$H_c = \frac{P}{S},$$

where P is the load in kg, and S is the area of the imprint in sq.mm.

The use of a cone instead of a sphere for measurement of the hardness resulted in a similarity between the imprints obtained and permitted the load used in the tests to be varied and the hardness values obtained under various loads to be subsequently compared. The load used for the measurement of hardness at room temperature was 60 kg. After their hardness has been measured, the cast specimens were pressed into rods, 11 mm in diameter. The degree of deformation was 80%, and the average length of the rods was 160 mm. The pressing was carried out in a 35-tonne hydraulic press at 250°. From the rods obtained, specimens were prepared for hardness, plasticity, and tensile measurements.

In order to determine the degree to which the alloys approximated to the equilibrium state and to determine the amount of annealing required for the attainment of equilibrium, various periods of annealing were given – from 2 hrs to 6 days – hardness determinations being made at intervals. We did not detect any characteristic points on the hardness curves for the unannealed alloys in the cast and deformed conditions.

TABLE

Composition of Alloys

Alloy No.	Atom % Cd	Wt. % Cd	Alloy No.	Atom % Cd	Wt. % Cd
1	0	0	16	52	82.3
2	10	33.9	17	54	84.4
3	20	53.6	18	56	85.5
4	23	58	19	58	86.5
5	25	60.6	20	60	87.3
6	26	64.2	21	62	88.3
7	33	69.5	22	67	90.2
8	35	71.3	23	70	91.5
9	39	74.4	24	72	92.2
10	40	75.5	25	73	92.3
11	42	76.9	26	75	93.3
12	44	78.4	27	77.95	94.2
13	46	79.98	28	79.5	94.7
14	48	81.0	29	85.0	96.3
15	50	82.2	30	90	97.6
			31	100	100

After the annealing, and with increase in its duration, minima began to appear on the hardness curves in places that corresponded to the composition of compounds. When deformed specimens of the alloy corresponding in composition to the compound MgCd had been annealed for 4 hrs, the hardness value (70-80 kg/sq.mm) did not change further with further heating at the annealing temperature. However, the hardness of alloys having the compositions of the other two compounds continued to change beyond this period and attained a constant value only after a 4-day annealing; this is to be explained, evidently, by the greater rate at which the compound MgCd attains equilibrium, as compared with the compounds Mg_3Cd and $MgCd_3$. In the process of bringing the alloys to equilibrium by annealing, there is an increase in hardness, due to an aging effect, of alloys having compositions approximating to the compounds Mg_3Cd and MgCd. The hardness curves determined at room temperature for alloys that have been annealed for 6 days show minima for compositions corresponding to each of the three compounds indicated, and they show the least scatter in the hardness values (see Fig.1, curve a).

On the basis of the results of these determinations, and also of those of previous investigations into the rates of change in the solid solutions of the given system [4,5,6,7], all the alloys were annealed for a period of 6 days; for 3 days annealing was carried out at 280° for the purpose of homogenization, and about a day was then given at a temperature somewhat (10-15°) less than the temperature of formation of each of the compounds. In choosing 280° as the homogenization temperature, we took into consideration the fact that the temperature must be high enough for all the alloys to pass into the solid solution region, but not so high as to cause appreciable evaporation in the most readily fusible alloys of the system. All the alloys were sealed for annealing in evacuated glass tubes. Annealing was carried out in a muffle furnace. The temperature was regulated by the aid of a potentiometer. Apart from the hardness measurements already mentioned, measurements of tensile strength and of plasticity under static and dynamic conditions were carried out at room temperature on the alloys that had been annealed for six days according to the procedure given above. The tensile tests were done on Gagarin's machine with autographic recorder, and the plasticity tests were done on a hydraulic press (static) and on a vertical impact tester (dynamic). The load used in the tests was kept constant, being 7 tonne in the static test, while the available work in the dynamic test was 8 kg.m (weight of striker 20 kg, fall 0.4 m). Thus in the compression tests the specimens were not taken to the destruction point; the specimens were of diameter 11 mm and of height 10 mm.

The tensile strength (kg/sq.mm) of the alloys was determined from the usual formula

$$\sigma_B = \frac{P}{F},$$

where P is the maximum load in kg, and F the cross-sectional area in mm just before break. The plasticity of the alloys was determined by the change in the height of the specimens (degree of settling) and was calculated from the formula:

$$\epsilon = \frac{h_0 - h_1}{h_0} \cdot 100\%,$$

where h_0 is the height of the specimen before the test (mm), and h_1 is the height of the specimen after the test (mm).

It will be seen from the results given that annealed alloys having the composition of chemical compounds are distinguished at room temperature by their low hardness and strength (Fig.1, curves a and b) compared with the other alloys of this system. It is curious that, when alloys approximating to compounds in composition are tested for behavior under compression, they show an enhanced plasticity (Fig.1, curves c and d). The maxima for hardness and strength and the minima for plasticity that are to be observed on the curves for these properties

The extent of the regions of these solid solutions is best defined by the results on the tensile strength of the alloys. It should be noted that in the present instance the solid solution regions are continuous, and, from the measurements of the mechanical properties, we were unable to detect the presence of transitional heterogeneous regions when passing, by changing the concentrations of the components, from one solid solution to another.

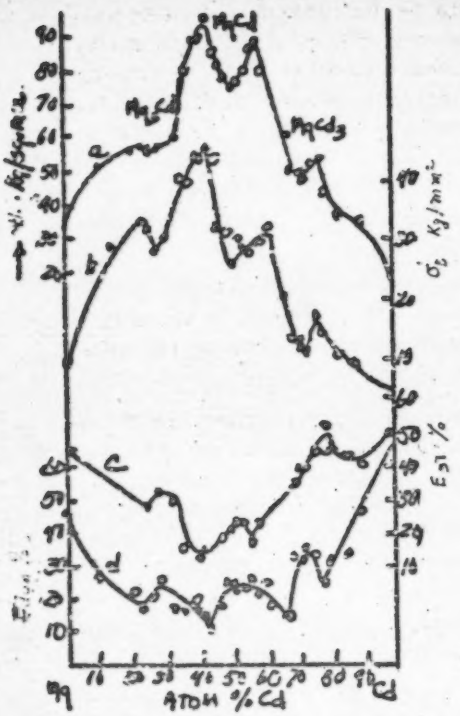

Fig. 1. Mechanical properties of alloys that have been annealed for 6 days: a) hardness; b) tensile strength; c) plasticity under static pressing; d) plasticity under dynamic pressing.

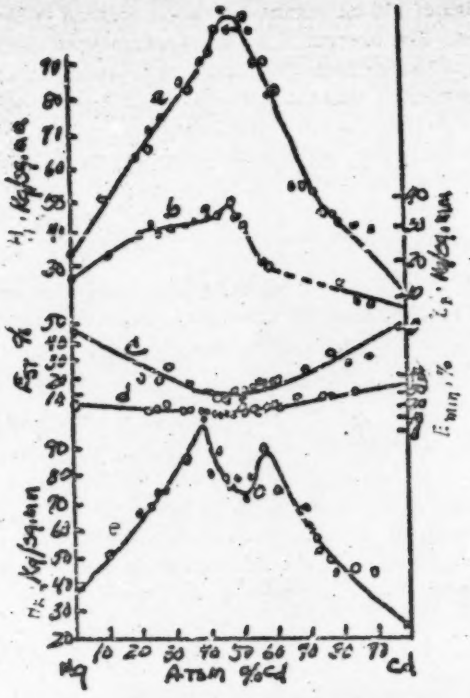

Fig. 2. Mechanical properties of quenched alloys: a) hardness of alloys quenched from 280°; b) tensile strength of alloys quenched from 280°; c) plasticity (static settling) of alloys quenched from 280°; d) plasticity (dynamic settling) of alloys quenched from 280°; e) hardness of alloys quenched from 200°

In order to determine the mechanical properties of the alloys of this system in the solid solution region, we carried out a quenching treatment from 280° with the object of fixing the solid-solution structure in the alloys. The quenching temperature was chosen in the same way as in the case of annealing — it must be sufficiently high for all the alloys to move into the solid solution region, but not too high, because of the tendency of the alloy components to evaporate. The alloys to be quenched were sealed in evacuated tubes and maintained at the quenching temperature for a day. The specimens were then quenched in water. On the specimens heat-treated in this way, measurements were made at room temperature of the mechanical properties that were determined before on annealed alloys. In order to avoid the possibility of the breakdown of the solid solution at room temperature, all the tests were carried out as soon as possible after the quenching treatment. Quenching was therefore done in small batches at a time; in the case of tensile tests, the quenching treatments on the specimens were carried out in succession. Hardness measurements were made not only on specimens quenched from 280°, but also on specimens quenched from 200°. The temperature for the formation of the compound MgCd is disputable, but the presence of this compound at 200° has been confirmed by all investigators of this system. The results obtained by tests at room temperature on specimens quenched from 280° and from 200° are given in Fig. 2, and it will be seen that there are no maxima or minima, indicative of chemical compound formation, to be observed on any of the curves for the mechanical properties of alloys quenched from 280°. The courses of the curves are typical for solid solutions.

The hardness and strength of the quenched alloys rise as the percentage content of either component rises from zero, and they attain maxima at about 46 atom % Cd. It should be noted that alloys having compositions corresponding to compounds have higher hardness and strength, and lower plasticity, than the corresponding annealed alloys. For example, the alloy containing 50 atom % Cd (the compound MgCd) had a hardness after quenching of 100 kg/sq.mm, which was reduced to 75-80 kg/sq.mm, i.e. by about 25%, when the alloy was annealed. The strength of this alloy was reduced by the annealing process by 45%, and the plasticity rose by 60-70%. When hardness measurements are made on alloys which have been maintained at 200° for a day and then quenched in water, a single minimum is to be observed at the point corresponding to the compound MgCd. Measurements of the mechanical properties of the annealed and quenched alloys were carried out also at raised temperatures. All the alloys were tested for hardness at 280°, and alloys of composition approximating to MgCd were tested also at 350°; all the alloys were tested for plasticity under dynamic conditions at 280°, and the tensile strength and efflux pressure were determined; also at 280°, for alloys approximating in composition to MgCd.

In the testing of annealed alloys at high temperature, they were brought to the required temperature and held there while on the machines for one hour; they were then tested by the method used at normal temperature. A protective medium was used in tests at 350°. The results of measurements of mechanical properties at high temperature are given in Fig.3.

The courses of the curves representing hardness and plasticity measurements on the alloys at 280° have the same character as the courses of the curves for alloys quenched from this temperature. As was to be expected, at 280° the hardness of the alloys is considerably less, and their plasticity considerably higher, than at room temperature for quenched alloys. The identical qualitative character of the curves representing the properties of alloys quenched from 280° and of the curves for measurements at 280° indicates that the disorder → order process that occurs when the temperature is lowered in alloys of this system proceeds comparatively slowly, and hence it is possible, in the present case, to make use of the quenching method and then measure the properties at ordinary temperature. When measurements are made of hardness at 350°, and of strength and efflux pressure at 280°, on alloys in the region of the compound MgCd, no special points (minima) corresponding to this compound are to be observed.

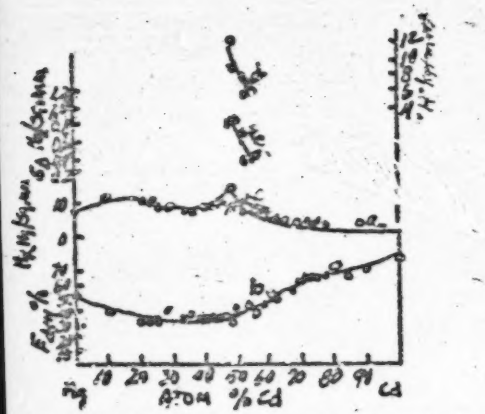

Fig.3. Mechanical properties of alloys at high temperature: a) hardness at 280°; b) plasticity (dynamic settling) at 280°; c) hardness at 350°; d) efflux pressure at 280°; e) tensile strength at 280°.

Investigation of the microstructure of the alloys confirmed the results of the mechanical tests. Thus, alloys corresponding in chemical composition to the compound MgCd which have been quenched from 280° (Fig.4, a) have the homogeneous structure of a solid solution. When this alloy has been annealed, slippage twinning occurs on the grains of the solid solution owing to the conversion of the solid solution into a chemical compound (Fig.4, b); this shows that the compound is formed below 280°.

SUMMARY

1. Mechanical properties of alloys of the magnesium-cadmium system in the annealed and quenched conditions have been measured at ordinary and at high temperatures for the first time.

2. By the method of mechanical tests on annealed alloys, it has been confirmed that the compounds Mg_3Cd, MgCd and $MgCd_3$ are present in the magnesium-cadmium system at room temperature.

3. The curves for the mechanical properties at 280 and 350°, and also the curves for alloys quenched from these temperatures, give no indication of the presence of the compound MgCd. It has therefore been shown that the compound MgCd is formed not from the melt, but from the solid solution, i.e., it is a typical Kurnakov compound.

4. The compounds Mg_3Cd, MgCd and $MgCd_3$ form considerable solid-solution regions and are distinguished

• See Plate, page 457-a.

by their high plasticity and low hardness, compared with the solid solutions from which they are formed.

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COORDINATION NUMBERS AND HYDRATION OF THE IONS Li^+, Na^+, K^+, Cl^-, Br^-, AND I^- IN AQUEOUS SOLUTIONS

O. Ya. Samoilov

It has been shown previously [1] that every water molecule in a solution of acid may on the average be represented as $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$, where e is the electronic charge and ϵ is a small positive charge associated with the presence in the water molecules of an excess proton. In this connection, measurement of the heats of solution of salts in acids, e.g. HCl, permits an evaluation of the coordination numbers of ions in aqueous solutions, i.e. the average numbers of water molecules that comprise the immediate surroundings of the ions in solution.

We have measured the heats of solution at 25° in aqueous solutions of HCl of various concentrations of the following salts: LiCl, NaCl, KCl, $NaBr\cdot 2H_2O$, $NaI\cdot 2H_2O$ and $N(CH_3)_4Br$. The measurements were carried out in a calorimeter having an isothermal jacket. The procedure used has been described previously [2]. The amounts of the salts taken for solution were such as to yield solutions containing about 0.05 mole of salt per 50 moles of water (in the case of NaCl — 0.17), i.e. so that the concentration was sufficiently small. For each salt, the final concentration of the solution was the same in all experiments.

The dehydration of lithium chloride (chem.pure, recryst.) was carried out by heating it in admixture with chem. pure ammonium chloride (to prevent hydrolysis) and then calcining to remove NH_4Cl completely. The hydrates $NaBr\cdot 2H_2O$ and $NaI\cdot 2H_2O$ were obtained by maintaining the salts (chem.pure, the sodium bromide was recrystallized) in a desiccator at room temperature (15-20°) over 44 and 59% sulfuric acid respectively until constant weight was attained.

The results obtained are given in Table 1. In this table the heats of solution in water of LiCl, NaCl and KCl according to the data of Lange [3] are given also (the figures are interpolated from Lange's data to the salt concentrations employed by us). In Figs 1 and 2 the relation between the heats of solution and the concentration of HCl in the solvent is shown. The curves are displaced along the ordinate axis, the same scale being retained for all the curves. The heats of solution L are given in kcal per mole of salt dissolving. The concentration of HCl (m) is expressed in moles HCl per 50 moles of water. Individual determinations of L are accurate within about 1%.

The heats of solution of the hydrates $NaBr\cdot 2H_2O$ and $NaI\cdot 2H_2O$ were measured, but the slopes of the curves obtained were precisely equal to the slopes of the curves for the anhydrous salts: the difference in heat of solution between the anhydrous salt and the hydrate for a given final salt concentration is constant and equal to the heat of hydration of the anhydrous salt. By the interpolation of the data of Wüst and Lange [3] for anhydrous NaBr and NaI to the concentration that we used, it is possible, with the aid of the determined heats of solution of $NaBr\cdot 2H_2O$ and $NaI\cdot 2H_2O$ in water, to determine the heats of hydration of anhydrous NaBr and NaI to the dihydrates. They are 4.64 and 5.95 kcal/mole respectively. It is known that the heat of hydration in aqueous solution is higher for Br^- than for I^-. The fact that the heat of hydration of the anhydrous salt to the dihydrate is lower for NaBr than for NaI emphasizes the impossibility of comparing heats of hydration of ions in the solid phase and in solution.

The curves obtained have a very low curvature, and the effect of HCl on the heats of solution of the salts may be characterized by the slopes $\Delta L/\Delta m$ of certain "averaged" straight lines. In so doing, the choice of units for the expression of the concentration is more or less arbitrary: the only thing that is essential for our further considerations is that weight units should be used. In Table 2 the values of β are given for the investigated salts $\left(\beta = -\frac{\Delta L}{\Delta m}\right)$, $\frac{\Delta L}{\Delta m}$ as found from the experimental data by the method of least squares. The values of β are expressed in cal/ mole per unit change in m.

With increase in the concentration of HCl in the solution in which dissolution of the salts under investigation is proceeding, there is an increase both in the concentration of H^+ ions, which corresponds to an increase in

TABLE 1

Integral Heats of Solution of Salts in Aqueous Solutions of HCl at 25°C

Salt Dissolved	Conc. of HCl (mole/50 mole H_2O)	Heat of Solution (kcal per mole salt)	Salt Dissolved	Conc. of HCl (mole/50 mole H_2O)	Heat of Solution (kcal per mole salt)
LiCl	0.00	+8.69	$NaBr \cdot 2H_2O$	0.83	−4.79
	0.00	+8.74*		1.69	−4.90
	0.50	+8.39		3.50	−5.16
	1.26	+8.14			
	1.26	+8.05			
	1.80	+7.84	$NaI \cdot 2H_2O$	0.00	−4.25
	2.58	+7.50		0.83	−4.34
	2.58	+7.50		1.68	−4.36
				2.37	−4.46
				3.47	−4.57
NaCl	0.00	−1.02			
	0.00	−1.03*			
	0.32	−1.14	KCl	0.00	−4.24
	0.32	−1.14		0.00	−4.26*
	0.76	−1.23		0.32	−4.31
	0.76	−1.24		0.33	−4.31
	1.14	−1.30		0.61	−4.31
	1.14	−1.29		0.77	−4.32
	1.72	−1.41		1.14	−4.34
	2.78	−1.64		1.72	−4.31
				2.70	−4.34
$NaBr \cdot 2H_2O$	0.00	−4.64			
	0.40	−4.76	$N(CH_3)_4Br$	0.00	−5.44
				0.81	−5.01
				1.64	−4.72

* According to Lange's data.

the positive charge of each molecule of water of the ions

of the ions $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$

in the solution [1], and also in the concentration of Cl^- ions. However, owing to the special nature of the hydrogen ion in aqueous solutions, only the increase in the concentration of H^+ ions has any effect on the heats of solution of the salts.

In actual fact, the interaction with ions of the dissolved salts of the greater part of the positive charges of the $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ ions is compensated by the negative charges of the Cl^- ions, for the solution as a whole is electrically neutral. However, the immediate surroundings of the hydratable cations (e.g. Li^+, Na^+) are composed mainly of water molecules. The same can be said of the surroundings of the anions (e.g. Cl^- for the dissolution of LiCl or NaCl). It will be assumed henceforth that the immediate surroundings of ions in aqueous solutions are always composed of water molecules only (which is in any case correct in dilute solution). In the first co-ordination layer of the ions, accordingly, only the positive charges of these molecules are present. A corresponding number of negative charges (Cl^- ions) are distributed outside the first coordination layer, but they have no effect on the heat of solution. The point is that the energy of their interaction with ions depends to an insignificant effect on the ionic radius. It may be assumed that it depends only on the ionic charge*, and interaction with cations of the dissolved salts is compensated by interaction with anions. Thus, the heat of solution of salts changes with increase in the concentration of acid in the solvent only as a result of the influence of increase in the effective positive charge of the water molecules that comprise the immediate surroundings of the dissolved ions. The slopes of the heat of solution curves are determined by the difference between the energies of interaction with cations and with anions. As these energies depend on the average numbers of water molecules comprising the immediate surroundings of ions, i.e. the coordination numbers of ions in solution, the possibility of the evaluation of these numbers emerges.

The energy of Coulomb interaction of the positive charges of the ions $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ in a solution of acid with cations and anions having unit charge may be written respectively:

$$E_c = -\frac{n_c \cdot e \cdot \epsilon}{R_c} \qquad \text{and} \qquad E_a = \frac{n_a \cdot e \cdot \epsilon}{R_a}$$

* Dependence on the radius is to be found only when the radius determines the distance between the particles. In liquids, where there is a rapid diminution in orderliness in the relative disposition of particles as the distance between them increases, the distribution of particles that are sufficiently far removed from one another is practically independent of their radii. The assumption that this dependence ceases to have effect already beyond the limits of the first coordination layer is, of course, a well known simplification.

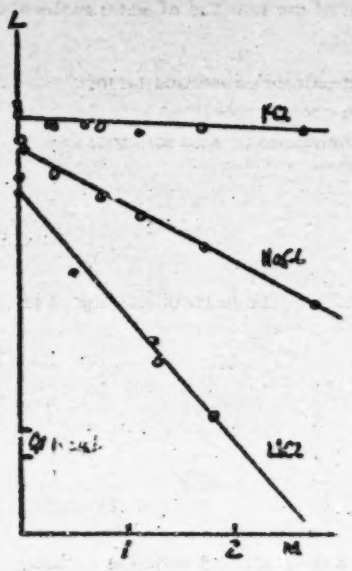

Fig. 1. Integral heats of solution of LiCl, NaCl and KCl in aqueous solutions of HCl: O — according to the results of the present work; ● — according to Lange's results.

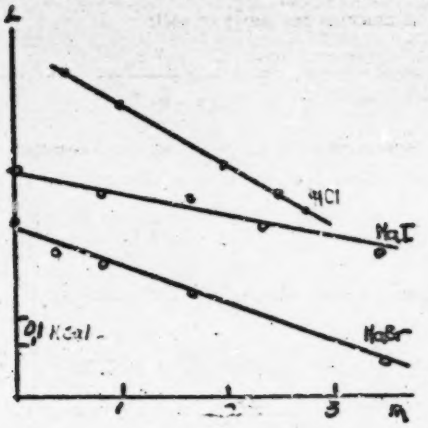

Fig. 2. Integral heats of solution of $NaBr \cdot 2H_2O$ and $NaI \cdot 2H_2O$ in aqueous solutions of HCl, and differential heats of solution of HCl: O — according to the results of the present work; ● — according to data in reference tables.

TABLE 2

Values of β for the salts investigated

Salt	LiCl	NaCl	NaBr	NaI	KCl
β	465	210	142	91	11

where n_c and n_a are the coordination numbers of the cation and anion in solution, e is the electronic charge, ϵ is the mean positive charge of the water molecules of the ions $\left|H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}\right|$ in a solution of acid (here one should speak of the effective value of ϵ), and R_c and R_a are the distances of the charge of the water molecules in the first coordination zones of the ions to the centers of the ions. The minus sign corresponds here to the repulsion of the positive charges from the cations of the dissolved salts (i.e. to a diminution in the exothermicity of the dissolution process).

We shall assume that the charge ϵ is related to the HCl concentration according to the equation $\epsilon = km$ (this, of course, follows from the model on which we have based all these considerations). As regards the coefficient k, it has in any case a constant value for low HCl concentrations, and, in this connection, the slopes of the $L-m$ curves should be compared for different salts at a given HCl concentration. However, the experimental results (an almost linear relation between L and m) indicate that the proportionality holds over a wide range of HCl concentrations. It is therefore permissible to compare the mean slopes of the curves ($\Delta L/\Delta m$). R_c and R_a are not known, owing to a certain indefiniteness in the position of the charge ϵ inside the water molecule and also of the orientation of the $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ ion with respect to the ions of the dissolved salts.

It is natural to equate R_c and R_a to $r_c + r_{H_2O}$ and $r_a + r_{H_2O}$, respectively, where r_c and r_a are the crystallographic ionic radii, and $r_{H_2O} = 1.38$ A, the radius of a water molecule. This, of course, amounts to an averaging-out of the position of the charge ϵ. It is not likely that this averaging process will lead to appreciable error: of the two orientations that can be assumed for the ion $H_{2+\frac{\epsilon}{e}}O^{\frac{\epsilon}{e}+}$ with respect to the ions of the dissolved salts, one corresponds to a value of R somewhat lower, and the other to a value somewhat higher, than $r + r_{H_2O}$.

Thus,

$$E_c = -\frac{n_c \cdot e \cdot k \cdot m}{r_c + 1.38} \cdot 10^8 \quad \text{and} \quad E_a = \frac{n_a \cdot e \cdot k \cdot m}{r_a + 1.38} \cdot 10^8 \qquad (1)$$

The factor 10^8 arises because E_c and E_a are expressed in ergs, while the radii of the ions and of water molecules are given in A.

By multiplying expression (1) by Avogadro's number N and by the erg-calorie conversion factor ($0.2389 \cdot 10^{-7}$), and by introducing the symbol K for $2.38 \cdot N \cdot e \cdot k$, we obtain the energy associated with the interaction between ions of the dissolved salts and the positive charges of water molecules in acid solutions expressed in calories per mole of salt:

$$E = -K\left(\frac{n_c}{r_c + 1.38} - \frac{n_a}{r_a + 1.38}\right) \cdot m, \quad K > 0.$$

In accord with the proposed interpretation of the effect of hydrogen ions on the heats of solution of salts, the heat of solution of a salt in a solution of HCl of concentration m is

$$L = L_0 + E = L_0 - K\left(\frac{n_c}{r_c + 1.38} - \frac{n_a}{r_a + 1.38}\right) \cdot m,$$

where L_0 is the heat of solution of the salt in water. Thus,

$$K\left(\frac{n_c}{r_c + 1.38} - \frac{n_a}{r_a + 1.38}\right) = \beta. \qquad (2)$$

Writing down the difference of such expressions (2) for two salts having identical anions, but different cations, we obtain

$$K\left(\frac{n_{c_1}}{r_{c_1} + 1.38} - \frac{n_{c_2}}{r_{c_2} + 1.38}\right) = \beta_1 - \beta_2. \qquad (3)$$

The expressions (2) and (3) make it possible to evaluate the quantities n_c and n_a. However, there is still the relation between the coordination number of the ions and their hydration to consider.

Coordination numbers cannot be used directly for the characterization of the hydration of the individual ions, since the sizes of the ions would not then be taken into account. In order to characterize the hydration it is necessary to examine the closeness of the distribution of water molecules around the ions. As a measure of hydration we may take the value of the surface density of distribution of water molecules in the first coordination layer of the ions.

$$\rho' = \frac{n}{4\pi(r + 1.38)^2}, *$$

where n is the coordination number of the ion, r is its radius, and $4\pi(r + 1.38)^2$ is the area of the first coordination sphere in Å^2. The value of ρ' for the individual ions may be compared with the corresponding value for water molecules in water:

$$\rho'_{H_2O} = \frac{n_{H_2O}}{4\pi R^2},$$

where n_{H_2O} is the mean coordination number of water molecules in water, and R is the mean distance between the centers of adjacent molecules in water. At 25° n_{H_2O} and R have the values, respectively, of 4.6 and 2.90 Å [4]**; $\rho'_{H_2O} = 0.044$ Å^{-2}.

It is expedient to characterize the hydration of ions by the density of the distribution of water molecules around them because the phenomenon of hydration in aqueous solutions manifests itself in the influence of the ion on the translatory motion of water molecules (principally the nearest water molecules). As we have previously shown [5], the density of distribution of particles in a liquid is related to their translatory movements. Increase in translatory motion corresponds to increase in the number of local rarefications in the liquid and therefore to a

* The prime is used to distinguish from the well known radial distribution function $\rho(r)$, which corresponds to a volume density.

** The radius of the first coordination sphere must here be definitely considered as equal to the mean distance between the centers of adjacent molecules in water, which has been measured with adequate accuracy by Morgan and Warren [4]. The crystallographic radii for the ions and water molecules are used owing to the absence of reliable measurements of the mean distances between the centers of the ions and the centers of the water molecules that are closest to them in aqueous solutions.

diminution in density; diminution in the translatory motion corresponds to an increase in density.

It has been shown that ions that undergo hydration increase the activation energy for the viscous flow of the neighboring water molecules, i.e. diminish their translatory motion [6,7] and hence for such ions

$$\rho^{*} \geqslant \rho^{*}_{H_2O} \qquad (4)$$

On the other hand, a number of ions (K^+, Cl^-, Br^-, I^-) increase the translatory motion of the neighboring water molecules (this case has been called negative hydration [7]). For such ions the following inequality must hold•:

$$\rho^{*} < \rho^{*}_{H_2O}. \qquad (5)$$

The inequalities (4) and (5) permit an evaluation of the lower limits of the coordination numbers of the ions that are hydrated and of the upper limits of the coordination numbers of the non-hydrating ions (negative hydration). Thus, $n_{Na^+} > 3.05$; $n_{K^+} < 4.02$; $n_{Cl^-} < 5.57$.

From a comparison of the values of β for NaCl and NaBr ($NaBr \cdot 2H_2O$), it is possible to indicate the lower limit of the value of K in the relations (2) and (3). Subtracting the expression (2) for NaBr from the corresponding expression for NaCl, we obtain:

$$K\left(\frac{n_{Br^-}}{3.34} - \frac{n_{Cl^-}}{3.19}\right) = 63, \qquad (6)$$

from which it will be seen that $n_{Br^-} > n_{Cl^-}$, since $K > 0$. On the other hand, a comparison of the heats of hydration of the ions Cl^-, Br^-, and I^-, and also of a number of properties of chloride, bromide, and iodide solutions, leads to the view that in this series the negative hydration of the ions increases. The inequality $\rho_{Br^-} < \rho_{Cl^-}$ must therefore hold, from which it follows that $n_{Br^-} < 1.096\, n_{Cl^-}$. Substituting this limiting n_{Br^-} in formula (6), we obtain $0.0147\, K \cdot n_{Cl^-} > 68$ or

$$K > \frac{68}{0.0147\, n_{Cl^-}}. \qquad (7)$$

We obtain the lower limit of K by substituting in formula (7) the upper limit of n_{Cl^-}. From the expression (2) for KCl it will be seen that $\frac{n_{K^+}}{2.71} - \frac{n_{Cl^-}}{3.19} > 0$, and since $n_{K^+} < 4.02$, therefore $n_{Cl^-} < 4.74$ (this figure is less than that given by the equation $\rho^{*}_{Cl^-} < \rho^{*}_{H_2O}$). Correspondingly $K > 976$.

We are now in a position to indicate the lower limit of n_{K^+}. From expression (3) for NaCl and KCl:

$$n_{K^+} = 2.71\left(\frac{n_{Na^+}}{2.36} - \frac{199}{K}\right),$$

from which it follows that $n_{K^+} > 2.95$, since $n_{Na^+} > 3.05$ and $K > 976$. From the expression (2) for LiCl it is possible to determine the upper limit of the coordination number of the lithium ion; it is 4.23.

If we make use of the slope of the curve for the dependence of the differential heats of solution of HCl on its concentration, the limits of possible values of n_{K^+} can be narrowed, and the value of K can be evaluated. The curve $-\Delta H, m$ for HCl, constructed from tabulated data [8], is given in Fig.2 (ΔH, it is true, refers to 18°). The value of $\beta = \Delta H/\Delta m$, calculated by the method of least squares, is 233 cal/mole per unit change in m.

The difference between the heat content of a mole of HCl in infinitely dilute solution and in a solution of concentration m is associated with the interaction of $H_{z+}\,\frac{\epsilon}{e}\,O^{\frac{\epsilon}{e}+}$ ions in the solution with chloride ions,

and also among themselves. It is not difficult to see that for low m the following equation, analogous to (2), is approximately obeyed for the curve constructed:

$$K\left(\frac{n_{H^+}}{R} - \frac{n_{Cl^-}}{3.19}\right) = 233, \qquad (8)$$

where n_{H^+} is the coordination number of water molecules $\left(H_{z+}\,\frac{\epsilon}{e}\,O^{\frac{\epsilon}{e}+}\right.$ ions$\left.\right)$ that do not enter into the immediate

• The peculiarities of water [5] are here of no significance since the distribution of the molecules around the ions is under consideration.

surroundings of the Cl^- ions. n_{H^+} must be taken as equal to the coordination number of water molecules in water (4.6 at 25°); $\underline{R}$ has the value 2.90 A (the mean distance between neighboring molecules in water according to the radial distribution curve) [4].

Subtracting equation (2) from (8), we obtain for KCl:

$$K\left(\frac{4.6}{2.90} - \frac{n_{K^+}}{2.71}\right) = 222, \qquad (9)$$

from which it follows that $n_{K^+} > 3.68$, since $K > 976$. Thus for n_{K^+} we have $3.68 \leq n_{K^+} \leq 4.02$. We will take n_{K^+} as equal to $\frac{3.68 + 4.02}{2} = 3.8$. Substituting this value of n_{K^+} in equation (9) we obtain $K = 1.17 \cdot 10^3$.

By evaluating K in this way from the determined experimental values of β by the aid of equations (2) and (3), we shall find the coordination numbers of the ions Li^+, Na^+, Cl^-, Br^-, I^-. The coordination numbers ($\underline{n}$) and also ρ' for these ions are given in Table 3.

TABLE 3

$\underline{n}$ (the Coordination Number in Aqueous Solution) and ρ' for the Ions Li^+, Na^+, K^+, Cl^-, Br^-, I^- at 25°

Ion	Li^+	Na^+	K^+	Cl^-	Br^-	I^-
n	3.8	3.7	3.8	4.4	4.8	5.3
ρ'	0.065	0.053	0.042	0.035	0.034	0.033

The values of $\underline{n}$ found are close to the mean coordination number of water molecules in water, which points to the determining significance of the structure of water for the structure of dilute ionic solutions. In this sense, the results of the present work do not differ essentially from the conclusions of Bernal and Fowler [9], who, on the basis of a calculation of the energy of the coordination by ions of the water molecules of the solution, considered that the coordination number of a singly charged ion in aqueous solution is four.

In conclusion I express my thanks to A. F. Kapustinsky for his cooperation in the performance of this work.

SUMMARY

1. The integral heats of solution of LiCl, NaCl, KCl, $NaBr \cdot 2H_2O$, $NaI \cdot 2H_2O$ and $N(CH_3)_4Br$ in aqueous solutions of HCl of various concentrations have been measured at 25° in a calorimeter with an isothermal jacket.

2. A thermochemical method for the evaluation of coordination numbers of ions in aqueous solutions has been developed. The coordination numbers of Li^+, Na^+, K^+, Cl^-, Br^-, I^- have been determined at 25°. In dilute solutions they are close to the mean coordination number of the water molecule in water.

3. The following expression is proposed as a measure of the hydration of ions; $\rho' = \frac{n}{4\pi(r + 1.38)^2}$, where $\underline{n}$ is the coordination number of the ion in solution, $\underline{r}$ and 1.38 are the radii (in A) of the ion and of the water molecule respectively, ρ' is the surface density of distribution of water molecules in the first coordination layer of the ions. For ions that undergo hydration $\rho' > \rho'_{H_2O}$, and for non-hydrating ions (negative hydration) $\rho' < \rho'_{H_2O}$.

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THE NATURAL SORBENTS OF THE FAR EAST

COMMUNICATION 1. ELECTRON-MICROSCOPIC INVESTIGATIONS OF NATURAL SORBENTS

V. T. Rykov, V. M. Lukyanovich, and L. V. Radushkevich

There is a wide distribution in nature of highly dispersed substances having a large internal (specific) surface that is accessible to vapors and liquids and may attain the area of tens or hundreds of square meters per gram of material; these we bring together under the general name of "natural sorbents". Natural sorbents, owing to their ready accessibility and low cost are widely used in industry. In the investigation of the quality of natural sorbents, we meet with the necessity of studying their skeletal structure, the degree of dispersion of the particles, and the structure of these particles.

For the main part, natural sorbents are complex polymineral formations with a varied structure in their component particles and in the nature of the surface of these particles. Adsorption investigations permit us to obtain an idea of the structure of the pores and the size distribution of the pores, and moreover, the application of the electron microscope to the investigation of the skeleton of the natural sorbents permits certain conclusions to be drawn concerning the degree of subdivision of the natural product, of the form of the particles that compose it, and of the character of the macro- and transitional porosity of the natural sorbent. Apart from this, electron-microscopic investigation of natural sorbents permits the observation of the mineralogical varieties composing the given natural sorbent and the estimation of their approximate proportions. Hence in embarking on a general investigation of the sorption properties and structure of natural sorbents, we made use of the electron-microscopic method of investigation.

In conjunction with chemical and thermographic analysis, the electron-microscopic method of investigation permitted, in many cases, the establishment or more precise determination of the mineralogical composition of the natural sorbent. The procedure used in the electron-microscopic investigations was as follows. The adsorbent powder was shaken up with water and allowed to stand, generally for $\frac{1}{2}$ or 1 hr, after which a drop of the suspension was applied to a collodion film, which served as a support. When it had dried, the preparation was examined in the electron microscope, and the most characteristic places were photographed.

Electron-microscopic Investigation of the Main Types of Sorbent

The natural sorbents comprise minerals of various composition and origin and of appreciable or high absorptive power. The following main typical varieties of natural sorbents may be distinguished:

a) ash tuffs and their weathering products;
b) decomposed agglomerate tuffs of old quaternary volcanos;
c) bentonite clays;
d) diatomites.

Ash Tuffs and their Weathering Products. Ash tuffs were formed as a result of the deposition of ash in water and did not later suffer migration, as a rolling tendency is not to be observed even in the detritus masses of psammitic tuff [1]. In their chemical composition, the ash tuffs are very homogeneous and may be considered to be analogs of the trachyliparites. The formation of ash tuff deposits belongs to the pliocene or upper miocene.

Weathering processes have affected ash tuffs in varying degree. In the photographs No. 1 and 2 of samples of ash tuff, particles of volcanic ash, 1-3μ across and with well defined edges, are visible; on these there are only slight signs of the formation of weathering products — hydrate forms of aluminohydrosilicates. In the photographs No. 3 and 4 of samples No. 18 and 17 of ash tuffs, the formation of hydrate forms of high porosity is now more readily visible. The formation of argillaceous minerals by the weathering of volcanic ash tuffs is confirmed also by the results of thermal analysis. The thermogram of sample No. 18 of ash tuff, the electron-microscope picture of which is given in Fig. 1, establishes the formation of halloysite (Fig.5), while for the ash tuff No. 17,

which shows a high degree of weathering under the electron microscope (picture No.4), the thermogram (Fig.6) indicates the presence of a mixture of the minerals halloysite and montmorillonite, identified by their characteristic endothermic effects, at 590° for the first, and at 695° for the second.

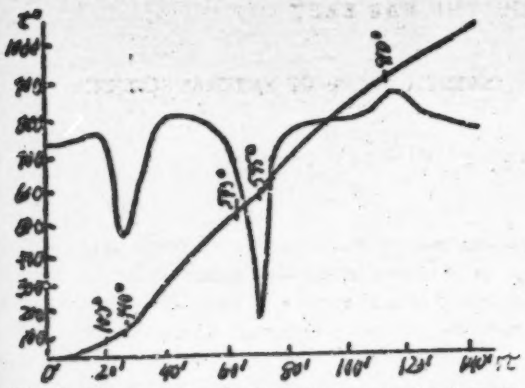

Fig. 5. Thermogram for Sample No.18 of Ash Tuff

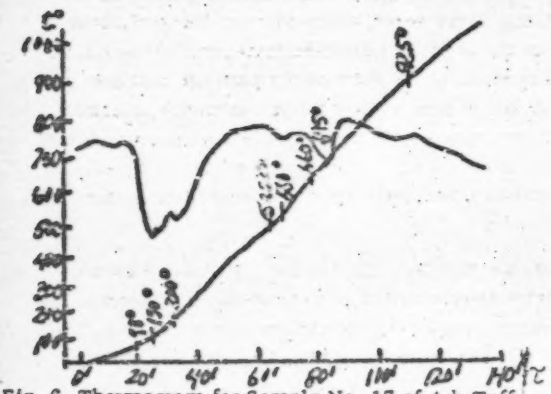

Fig. 6. Thermogram for Sample No. 17 of Ash Tuff

The process of disintegration in particles of volcanic ash is seen particularly clearly in photograph No.7, in which a single grain of volcanic glass has undergone surface disintegration with formation of fissures and translucent plates of argillaceous minerals. In photograph No.8 of a sample of decomposed tuff No. 20, there can be seen large numbers of platelike crystals of montmorillonite and characteristic "curls" of montmorillonite. The formation of montmorillonite and halloysite from volcanic glass in ash tuffs leads to increase in the specific surface of these minerals and to a rise in the limiting sorption values of vapors.

The table shows the results of determinations of the specific surface and of the limiting sorbed volume of benzene, obtained by one of us in a vacuum sorption apparatus [2].

Decomposed Agglomerate Tuffs. Geological investigations have brought to light a number of old-quaternary volcanos, the slag cones of which serve as sources of porous, spongy tuff material [3]. Slag cone material (agglomerate), to an extent that depends on the amount of weathering that occurs under the influence of atmospheric reagents (water and carbon dioxide), undergoes decomposition with formation of aluminohydrosilicates, i.e. clay-like minerals.

In the course of the weathering process, deposits of argillaceous minerals are formed in the pores of the agglomerate; the agglomerate becomes more open in structure, and, as the decomposition process proceeds, a powder is formed, known as decomposed agglomerate tuff. Decomposed agglomerate tuffs are characterized by fairly high adsorption properties (see table). The electron-micrographs Nos. 9, 10, 11, 12 of samples of decomposed agglomerate tuffs show the high dispersion of the constituent particles and the conversion of a considerable part of the volcanic glass into the argillaceous mineral montmorillonite. The high degree of dispersion of the particles of the decomposed agglomerate tuff No. 87 is in agreement with the high sorption properties of this tuff, which in its qualities as a sorbent is superior even to activated gumbrin.

Bentonite Clays. It has been possible to establish by means of the electron microscope that samples of these clays are composed of coarsely lamellar montmorillonite (photographs No.13 and 14). Without activation, their absorptive power is not great, but chemical activation leads to a sharp rise in sorptive capacity. In contrast to polymineral formations, such as the decomposed agglomerate tuffs, bentonite clays consist mainly of montmorillonite, as can be seen from a large number of electron-microscope observations that we have made (unfortunately, limitations of space prevent us from showing these photographs).

In some cases the electron microscope permits the ready identification of argillaceous minerals, if they are of the montmorillonite type. For example, in photograph No. 15, which is of a sample of kaolin from Glukhov*, , crystals of kaolinite of pseudohexagonal form are excellently visible, and it can be seen that the whole mass of the clay consists of these crystals. Examples of the determination of the mineralogical composition of clays by means of the electron microscope are given in a paper by Vikulova [4].

*The sample of kaolin was presented by M. L Kuadzhe, to whom the authors express their indebtedness.

Fig. 1. Ash tuff No. 18 (X 8000).

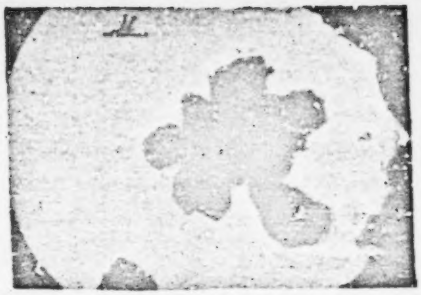

Fig. 2. Ash tuff No. 18 (X 8000).

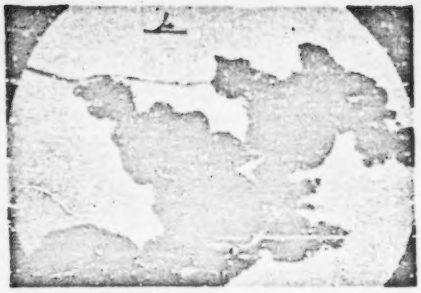

Fig. 3. Ash tuff No . 19 (X 8000).

Fig. 4. Ash tuff No. 17 (X 8000).

Fig. 7. Grain of volcanic glass from sample of decomposed tuff No. 20 (X 10,600).

Fig. 8. Sample of decomposed tuff No. 20 (X 8000).

Fig. 9. Decomposed agglomerate tuff No. 83 (X 8000).

Fig. 10. Decomposed agglomerate tuff No. 87 (X 8000).

Fig. 11. Decomposed agglomerate tuff No. 95 (X 8000).

Fig. 12. Decomposed agglomerate tufs No. 173 (X 8000).

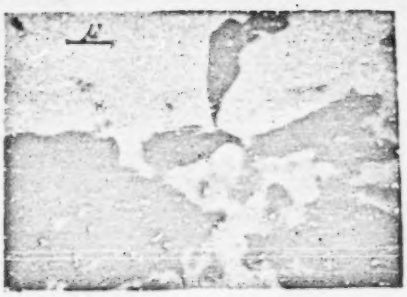

Fig. 13. Sample No. 42, Montmorillonite clays (X 8000).

Fig. 14. Sample No. 13, Montmorillonite clays (X 8000).

Fig. 15. Sample of kaolin (X 8000).

Fig. 16. Diatomaceous sludge from sea bottom, 820 m deep, No. 161 (X 8000).

Fig. 17. Diatomaceous sludge from sea bottom, 820 m deep (X 8000).

TABLE

Sorption Properties of Natural Sorbents

Name of samples	Volume of sorbed benzene (cc/g)		Specific surface of the sorbent skeleton S (sq.mm/g)
	at the pt. at which hysteresis begins	at complete saturation	
Ash tuffs No. 18	0.018	0.136	40
" No. 19	0.021	0.087	34
" No. 17	0.013	0.141	26
" (decomposed) No. 20	0.014	0.164	60
" " No. 130	0.017	0.147	55
Decomposed agglomerate tuffs No. 87	0.027	0.369	87
" " " No. 88	0.099	0.844	195
" " " No. 95	0.031	0.162	57
" " " No. 173	0.044	0.290	76
Bentonite clays No. 42	0.025	0.179	40
Kaolin clay No. 77	0.060	0.276	78
Diatomites No. 81	0.019	0.323	26
" No. 142	0.018	0.176	29
Diatomaceous sludges No. 161	0.007	0.133	15
" " No. 162	0.005	0.110	9

Diatomites and Diatomaceous Sludges. The identification of diatomites can be carried out very effectively by means of the electron microscope, the remnants of the siliceous diatom skeletons being readily visible. The diatomites investigated by us (tests No. 81 and 142) also showed the presence of remnants of the siliceous skeletons of diatomaceous algae. When investigating the sorptive properties of diatomites and of modern diatomaceous deposits (sludges), we incidently obtained photographs of diatomaceous sludges*, parts of which are given in Fig. 16 and 17. These are photographs of diatomaceous deposits taken from a depth of 820 m at the bottom of the sea at horizons of 43-45 and 175-178 cm. Such photographs should be of great interest to paleobotanists. A detailed examination in the electron microscope of diatomites and modern diatomaceous deposits indicates the greater opalization of the siliceous skeletons in the diatomites, evidently because of the greater sorptive power of the latter, as compared with diatomaceous sludges (see Table).

SUMMARY

1. Electron-microscopic investigation of natural sorbents has permitted qualitative observations to be made concerning the character of the subdivision of the basic material composing the mineral, has enabled certain quantitative ideas concerning the dimensions of the particles, i.e. the degree of dispersion, to be obtained, and, in conjunction with knowledge of the chemical composition and with the thermal analysis, has, in many cases, indicated the basic mineral formations composing the given natural sorbent. For monomineral material, the mineralogical composition can be very readily determined.

2. Further work must be directed to the development of a procedure for separating polymineral substances into their separate components, which must be compared with standard samples of monomineral substances (kaolinite, halloysite, montmorillonite, etc.) of definite composition and structure in order to give a quantitative idea of the mineralogical composition of the natural sorbent under investigation.

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* The samples of diatomaceous sludges were obtained by us from P. L. Bezrukov, to whom the authors are very grateful.

THE EFFECT OF ALTERNATING CURRENT ON THE ELECTRODEPOSITION OF NICKEL

A. T. Vagramyan and A. A. Sutyagina

Alternating current is widely used in the study of various kinds of electrochemical processes, and also for effecting or improving a number of technological processes. Thus, alternating current is used in the study of the structure of the electrical double layer [1], for the elucidation of the kinetics of the formation and dissolution of oxide films [2], in the study of the discharge and ionization of hydrogen [3], and also for the anodic dissolution of various metals (Cr, Mn, Pt, etc.) [4].

Studies have been made in a number of papers of the effect of the superposition of an alternating current on the cathodic process in the electrodeposition of metals. Thus, Izgaryshev, Kudryavtsev, and Berkman [5], Kohlschutter and co-workers [6], and others have noted a considerable reduction in the polarization of the cathode in the electrodeposition of nickel. There are also papers showing that the superposition of an alternating current during the electrodeposition of metals greatly affects the structure of the deposit [6,7]. In spite of these investigations on this subject, the causes of the change in structure of electrolytic deposits and of the reduction in the degree of polarization of the electrode remain obscure. In the present investigation, some supplementary data concerning the effect of an alternating current on the electrodeposition of nickel are brought forward.

EXPERIMENTAL

In our study of the effect of alternating current on the structure of electrolytic deposits of nickel we used the following circuit (Fig.1); AC is an accumulator, C a condenser, mA d.c. and a.c. milliammeters, R_1 and R_2 rheostats, Dp a choke, E the source of a.c, A the anode, K the cathode, and B an auxiliary nickel electrode for the superposition of the alternating current. Electrodeposition of nickel was carried out from electrolyte of the following composition:

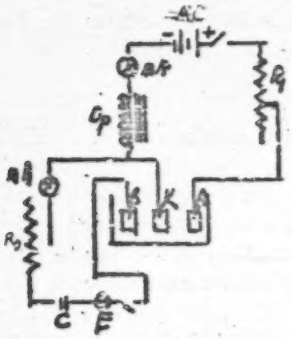

Fig. 1

$NiSO_4 \cdot 7H_2O$	250 g/liter
NaCl	5 g/liter
H_3BO_3	30 g/liter
pH	5,4-6

The temperature of the electrolyte was 20°.

For the electrodeposition of nickel the density of the direct current was varied from 1 to 3 amp/sq.dm, and the density of the superimposed alternating current was varied also from 1 to 3 amp/sq.dm. The structures of the electrolytic deposits of nickel, as exhibited by the electron microscope "replica" method (magnification 7000), are shown in Figs. 2,3 and 4*. The frequency of the alternating current was 50 cycles/sec. Fig. 2 shows the structure of a nickel deposit obtained at a direct current density of 2 amp/sq.dm without superimposed a.c. The deposit shown in Fig.3 was formed at a direct current density of 2 amp/sq.dm with superimposed 50 cycles/sec a.c. of the same density. For the deposit shown in Fig.4, the d.c. density was 2 amp/sq.dm and the a.c. density was 3 amp/sq.dm.

As will be seen from the photographs, in the range of a.c. density 1-2 amp/sq.dm there is no appreciable increase in the size of the crystals of the deposit, but at an a.c. density of 3 amp/sq.dm the grain size increases sharply. It is evident that this increase in crystal size is to be observed only when the value of the superposed alternating current exceeds that of the direct current.

Besides studying the structures of electrolytic deposits of nickel, we examined the effect of the super-

* We express our gratitude to A. B. Shekhter and I. I. Tretyakov for the determination of the microstructures of the deposits with the aid of the electron microscope. See Plate, p. 547.

position of an alternating current on the porous character of the deposits. In these investigations electrolytic deposits of nickel were obtained from electrolyte of the same composition of a d.c. density of 2 amp/sq.dm, the a.c. density being varied from 1 to 3 amp/sq.dm. The thickness of the deposit investigated was 18-20 μ. The number of pores was determined by the aid of a reagent of the following composition:

$K_4Fe(CN)_6$ . . . . . .20 g/liter
NaCl . . . . . 10 g/liter

The reagent was allowed to act for 2 min. The pores were counted under the microscope at a magnification of 50 [8]. The experimental results are given in Table 1.

TABLE 1

Dependence of the Pore Density* on the Relative Densities of the Direct and Alternating Currents (frequency of a.c, 50 cycles/sec)

D.c. density (amp/sq.dm)	A.c. density (amp/sq.dm)			
	0	1	2	3
	Number of pores per sq.cm			
1	20	8	10	16
2	14	8	9	14
3	16	7	11	13

* The pore density results given in Table 1 are average values from 18 experiments.

TABLE 2

Dependence of Pore Density on the Frequency of the Alternating Current

D.c. density (amp/sq.dm)	A.c. density (amp/sq.dm)	A.c. frequency (cycles/sec)					No. of pores per sq.cm without superposition of a.c.
		20	50	500	4000	12000	
		Number of pores per sq.cm					
1	1	7	8	10	17	18	20
2	1	7	8	11	14	13	14
3	1	9	8	8	14	15	16

As will be seen from these results, when an alternating current of density of 1-2 amp/sq.dm is superimposed, the number of pores diminishes sharply. Besides studying the effect of the density of the alternating current, we investigated the effect of the frequency of the current on the porous nature of the electrolytic deposits of nickel. Table 2 shows the dependence of the pore density on the frequency of the alternating current. As will be seen from Table 2, a high-frequency alternating current has no effect on the pore density of electrolytic deposits of nickel.

DISCUSSION OF RESULTS

It is evident that, when there is a superimposed alternating current of density greater than that of the direct current, conditions are created at the cathode that lead not only to intensive growth in the nickel crystals formed, but also to their periodic dissolution in association with the changing direction of the alternating current. If it is assumed that the electrolytic deposit on the cathode consists of crystals of variable size (which is indeed so in most cases, see Fig.2), then it may be supposed that when the direction of the current changes there will be preferential dissolution of the fine crystals, owing to their greater excess of surface energy and therefore lower stability when compared with the larger crystals.

The dependence of solubility on surface energy and on crystal dimensions is given by Thomson's equation:

$$RT \ln \frac{p_2}{p_1} = \frac{2\sigma M}{d} \cdot \frac{1}{r_2} - \frac{1}{r_1}, \qquad (1)$$

where p_2 is the vapor pressure of crystals of radius r_2, p_1 is the vapor pressure of crystals of radius r_1; σ is the surface tension of the crystals, M is the molecular weight, and d is the density of the metal. Denoting the L.H.S. of equation 1 by η, the overvoltage, [8] and assuming r_1 to be sufficiently great, we obtain:

$$\eta = \frac{2\sigma M}{dnF} \cdot \frac{1}{r_2}. \qquad (2)$$

The determination of the dissolution rates for crystals of various dimensions from this formula is difficult, firstly owing to the absence of exact data on the surface tension of the crystals of solid metal, in particular nickel, and secondly owing to the difficulty of establishing the exact relationship between the overvoltage and the crystal dimensions.

Analogous calculations from equation 2 for the deposition of silver [9] have shown that for a ten-fold change in crystal dimensions ($r' = 1.4 \cdot 10^{-5}$ and $r'' = 1.4 \cdot 10^{-4}$), the overvoltage for silver deposition changes by only 1.7 mV. When it is considered that the order of magnitude of the overvoltage for dissolving nickel crystals scarcely changes in comparison with that of silver with variation in crystal dimensions, it is evident that the overvoltage arising from differences in the crystal dimensions in nickel is very small in comparison with the total overvoltage observed in the electrodeposition of nickel [10]. It may therefore be considered that variations in the rate of dissolution of crystals due to variations in size cannot play an important part in the electrodeposition of nickel, and it is thus impossible to explain the increase in size of nickel crystals when alternating current is superimposed as the result merely of preferential dissolution of small crystals.

Another possible explanation is as follows. When electrodeposition of nickel occurs in the course of electrolysis, there occurs the discharge not only of nickel ions, but also of hydrogen ions, with the result that colloidal particles of hydroxide are formed directly at the surface of the electrode, particularly in neutral or weakly acid solutions [11]. These particles, which separate at the cathode together with the depositing metal, act as passivators, hindering the growth of the nickel crystals. As a result of this inhibition of crystal growth, a finely crystalline nickel deposit is obtained. According to Billiter [12], these particles (passivators) may be detected in the form of black embedded matter at the boundaries of the grains by examination of metallographic preparations of the deposit.

The formation of finely crystalline deposits of nickel resulting from the action of the hydroxide, which is formed at the cathode and becomes embedded in the deposit, has been noted also by other authors [13]. In fact, when the nickel deposit is analyzed, a certain amount of oxygen can be detected, which confirms that the embedding of hydroxide in the deposit has occurred [12-14].

On the basis of the above discussion it may be regarded as probable that the formation of a finely crystalline structure in the electrodeposition of nickel is due to inhibition of crystal growth. The superposition of alternating current in the electrodeposition of nickel must reduce the effect of these passivators, since the electrode is polarized alternately cathodically and anodically — when polarization is anodic, the hydroxide particles not only cannot separate at the electrode owing to their positive charge, but will even move away from the electrode. On the other hand, owing to the anodic polarization of the electrode, the discharge of hydroxyl ions will occur there, leading to acidification of the solution adjacent to the electrode. Increase in the acidity of the layer adjacent to the cathode will result in the destruction of the hydroxide particles that have formed. These two processes will result in a reduction in the concentration of the hydroxide, i.e. of the inhibitor of crystal growth.

The high overvoltage value for the electrodeposition of nickel is to be explained by the difficulty, due to the inhibiting effect of adsorbed nickel hydroxide on the electrode surface, of discharging nickel ions [10]. The lowering of the overvoltage by the superposition of alternating current is to be explained by the partial removal of the nickel hydroxide.

On the basis of this discussion it is evident that, as the factors causing passivation of the crystals are removed, conditions are created that encourage the growth of individual crystals, and the factors preventing coalescence of crystals are removed also. Curtailment of the growth of a group of growing crystals appears to be one of the causes of the formation of pores between them [8].

Reduction in the number of pores when alternating current is superimposed is to be explained by a reduction in the adsorption of the passivators (nickel hydroxide) that inhibit the growth and coalescence of the growing crystals and prevent the formation of more compact deposits. The absence of any effect due to the alternating current on the number of pores in electrolytic deposits of nickel when the frequency is increased may be explained by the fact that at high frequencies the composition of the solution in the cathodic layer does not alter — acidification and the removal of hydroxide particles from the cathode layer do not occur owing to the high frequency with which the direction of the current changes [15].

SUMMARY

1. The effect of alternating current on the electrodeposition of nickel has been studied. It has been shown that, when alternating current of greater than a certain density is superimposed, the deposit is of a coarsely crystalline structure.

2. It has been shown that, when alternating current is superimposed, the number of pores in electro-

lytic deposits of nickel is reduced. With increase in the frequency of the alternating current, its effect gradually disappears.

3. A hypothesis is given in the paper concerning the possible mechanism of the action of alternating current on the structure of the deposit and also on the overvoltage for the discharge of nickel ions.

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A STUDY OF OXYGEN EXCHANGE ON VANADIUM CATALYSTS BY THE USE OF O^{18}

L. Ya. Margolis and E. G. Plyshevskaya

Several papers have appeared recently in the literature concerning the application of heavy oxygen to the study of the mechanism of oxidation reactions. Karpacheva and Rozen [1] consider that the ability of catalysts to undergo oxygen exchange is related to their catalytic activity. In investigations of oxygen exchange on copper oxide, manganese dioxide, and vanadium pentoxide at 200-450° they established that in all these cases oxygen exchange occurs. In 1940 Morita [2] published work in which he showed that on manganese dioxide at 400° there is oxygen exchange amounting to about 20%, but on copper oxide there is no oxygen exchange to be observed up to temperatures of 600-900°. In 1949 Allen and Lander [3] investigated oxygen exchange on copper (II) oxide, cobalt (III) oxide, and nickel (II) oxide, which were prepared by oxidation of metal foil with a mixture of O^{16} and O^{18} (O^{18} content of mixture: 1.4%), and they established that oxygen exchange begins at 600° on cobalt oxide and at about 400° on copper oxide. The authors maintained that there is a parallelism between the degree of oxygen exchange and the active surface of the catalyst.

On the other hand, Vaynshtein and Turovsky [4] in a study of the oxidation of carbon monoxide at MnO_2 asserted that oxygen exchange does not occur on a carefully dehydrated catalyst at 280°. Also, no exchange was detected with the reaction product — carbon dioxide. They explained the divergence between their results and those of Karpacheva and Rozen by the use by the latter of catalysts that had not been sufficiently freed from moisture. Presence of moisture in the catalysts facilitates oxygen exchange and makes it difficult to establish the true mechanism of the reaction. Owing to the existence of such contradictory data in the literature, it was essential, before studying the fundamental mechanism of the oxidation of hydrocarbons, to determine the degree of oxygen exchange on oxide catalysts of mild and severe oxidative effect. Oxygen exchange was studied at the temperature and for the time used in the oxidation reaction (350-450°).

EXPERIMENTAL

The exchange was studied under static conditions in the apparatus shown in Fig. 1. The gas passed from the gas collectors 31-35 into the manifold 3, and was introduced via the tap 10 into the reaction vessel 23. The latter was situated in an electric furnace 24, the temperature of which was maintained constant within 0.1° by the aid of a thermoregulator working in conjunction with a resistance thermometer.

The procedure was as follows: A weighed amount of catalyst (1-1.5 g) was placed in the reaction vessel, protected by means of solid carbon dioxide from grease vapor, and activated for several hours at 450°. The temperature required for the experiment was then established, and the catalyst was maintained at this temperature for an hour.

Heavy oxygen was obtained by the electrolysis of heavy-oxygen water, containing 0.9% O^{18}. The analysis of the oxygen was carried out before and after the exchange in the mass spectrometer. The oxygen was first mixed with carbon monoxide and burnt at a platinum wire in the reaction vessel 19 to give carbon dioxide, which was frozen out by means of liquid nitrogen in the tubes 28, which were fused off from the apparatus and placed in the mass spectrometer. As a result of the analysis, the enrichment of the carbon dioxide in $CO^{16}O^{18}$ in comparison with natural CO_2^{16} was determined. The enrichment coefficient for the orignal heavy oxygen was 2.35. The results of the mass-spectrometric analysis were accurate within 3-5%.

The exchange experiments were carried out by two methods:

1. Oxygen $O^{16} + O^{18}$ (0.9% O^{18}) was sorbed at catalyst that did not contain heavy oxygen. When sorption was complete, the residue of oxygen was pumped out, oxygen O^{16} was introduced into the gas phase, and this was maintained over the catalyst for 2 hrs.

2. Heavy oxygen was introduced into the catalyst by treating it with the vapor of heavy oxygen water at 450-500° in an apparatus for dynamic treatments. The O^{18} content of the catalyst was about 100 γ per g. This catalyst was maintained in an O^{16} atmosphere for 2 hrs. The reproducibility of the analytical results in the different experiments was quite satisfactory (see Table 1).

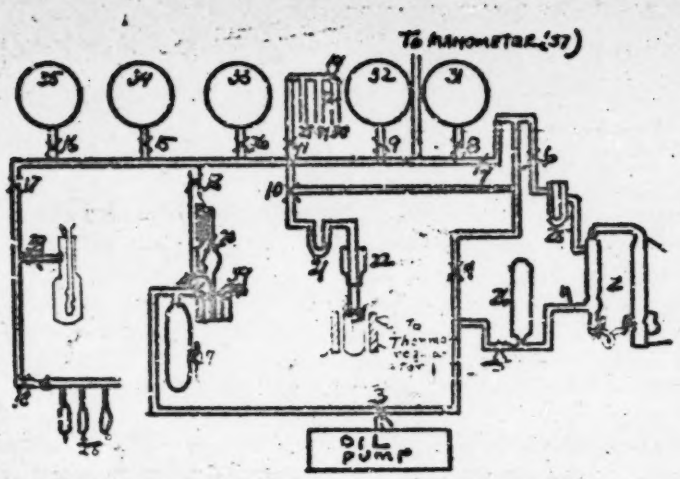

Fig. 1. Diagram of static apparatus for the study of oxygen exchange and the oxidation of hydrocarbons with heavy oxygen: 1) oil fore-pump; 2) mercury diffusion pump; 3) manifold; 4-18, 36-40) stop-cocks; 19) reaction vessel for burning O_2 + CO; 20) McLeod gage; 21,22,25) traps for freezing out; 23) reaction vessel; 24) electric furnace; 26,27) fore-vacuum reservoirs; 28) tubes for freezing out CO_2; 25,29,30,41) traps for analysis; 31-35) gas collectors

Various oxidation catalysts were used:

1) V_2O_5, chemically pure, having the rhombic lattice parameters: a = 11.7; b = 4.36; c = = 3.56, (according to Ketelaar [5]: a = 11.48; b = 4.36; c = 3.55.

2) V_2O_3 prepared by the reduction of vanadium pentoxide in a stream of hydrocarbon for 420 min.

V_2O_4 has a tetragonal lattice having the parameters: a = 4.51; c = 2.87. The data in the reference book (Strukturberichte) are a = 4.54, c = 2.88.

3) Magnesia-chrome catalyst: $MgCr_2O_4$ + MgO.

1. Sorption of Oxygen

In the work of Karpacheva and Rozen [1], a relation was found between oxygen exchange and activated sorption. The authors supposed that activated sorption is probably a stage of the exchange process, and they brought forward data concerning the parallelism between the degree of sorption and the extent of oxygen exchange. The extent of the exchange is closely related to the mobility of oxygen in the lattice and to the catalytic activity of the material. Therefore, in connection with an investigation of oxygen exchange on catalysts of mild and severe oxidative effect it is desirable to study the sorption of oxygen on them at the temperatures of the oxidation reaction. The isotherms for the sorption of oxygen on V_2O_5 and V_2O_3 for 250, 350 and 450° are given in Figs. 2,3,4 and 5. At these temperatures the sorption of oxygen is irreversible (Fig.6); the character of the isotherms shows that activated sorption of oxygen occurs on all these catalysts.

TABLE 1

Reproducibility of Results on Oxygen Exchange on Vanadium Pentoxide

No.	Catalyst	Temp. °C	Enrichment coefficient $CO^{18}O^{16}/CO_2^{16}$	Note
1	V_2O_5	350	1.0	Enrichment coefficient of original $CO^{18}O^{16}$ = 2.36
2	Ditto	350	1.0	
3	V_2O_5 containing O^{18} (100 γ/g)	350	1.0	
4	Ditto	350	1.0	
5	"	450	1.04	
6	V_2O_5 having sorbed O^{18} . . .	450	1.04	
7	V_2O_5 containing O^{18} (100 γ/g)	450	1.05	
8	Ditto	450	1.05	

We have previously [6] studied the sorption of oxygen on magnesium chromite, a typical catalyst for far-reaching oxidation of hydrocarbons. For this catalyst we found a relation between the activation energy and the degree of sorption. The distribution of surface sites in accordance with their activation energies obeyed an exponential law. If we represent the kinetic sorption curves obtained for the sorption of oxygen on V_2O_5 in bilogarithmic coordinates (log q, log t), all points are found to lie on a straight line over a range of times extending over three orders of magnitude (Fig. 7). In other words, the kinetics of the activated sorption of oxygen follow

Benham's equation

$$q = At^{1/n},$$

where $1/n = \alpha RT$

$$\therefore \quad A = f(T)$$

or

$$A = \frac{H}{\alpha(\tau_0)^{1/n}},$$

where τ is time; n and H are constants; R is the gas constant; T is the temperature;

$$\tau = \frac{1}{k_0 p^s},$$

where k_0 is a factor that enters into the rate constant; and p is the pressure.

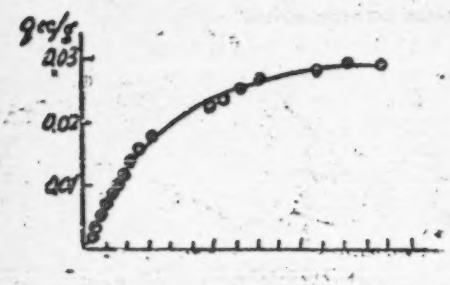

Fig.2. Isotherm for sorption of oxygen on V_2O_5 at 250°

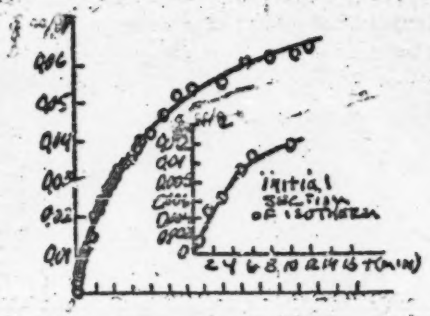

Fig.3. Isotherm for sorption of oxygen on V_2O_5 at 350°

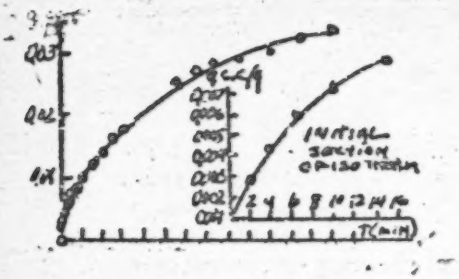

Fig.4. Isotherm for sorption of oxygen on V_2O_5 at 450°

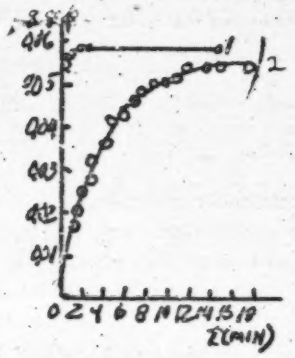

Fig.5. Isotherm for sorption of oxygen on V_2O_5 at 350°: 1) dehydrated, 2) in present of moisture

As Roginsky has shown [7], this is the typical kinetic equation for activated sorption on a heterogeneous surface characterized by an activation energy distribution function of exponential form for the adsorption process. In Fig.3 the distribution function $\rho(E)$ is expressed in terms of the logarithm to base 10 of time, the change of which is proportional to the change in activation energy for the process of activated sorption: $E \approx RT \log t$.

The number of active sites rises with increase in the activation energy both for $MgCr_2O_4$ and for V_2O_5 (see Fig.8 and 9, curves 1 and 2). The rate of sorption of oxygen on V_2O_4 is considerably greater than on V_2O_5. In Fig.4 and 5 the isotherms of sorption of oxygen on V_2O_5 and V_2O_4 at 450° are given. Vaynshteiin and Turovsky point out that presence of moisture in the pores of the catalyst considerably facilitates oxygen exchange between the catalyst and the gas phase at 180-200°. It was necessary to determine the effect of moisture in the catalyst on the sorption of oxygen.

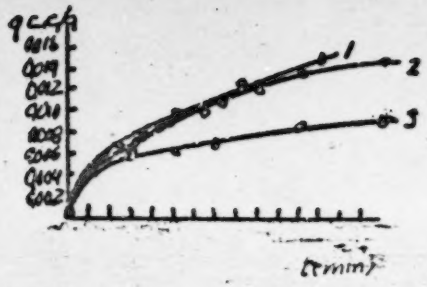

Fig. 6. Reversibility of sorption of oxygen on V_2O_5 (low activity) at 300°; 1) sorption isotherm (expt. 1) 2) sorption isotherm for oxygen in presence of moisture, 3) sorption isotherm (expt. 2)

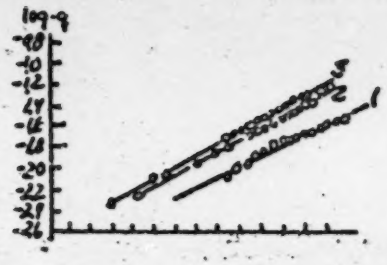

Fig. 7. Sorption isotherms for oxygen at V_2O_5 in bilogarithmic coordinates (log q and log t): 1) sorption isotherm at 250°, 2) sorption isotherm at 350°, 3) sorption isotherm at 450°

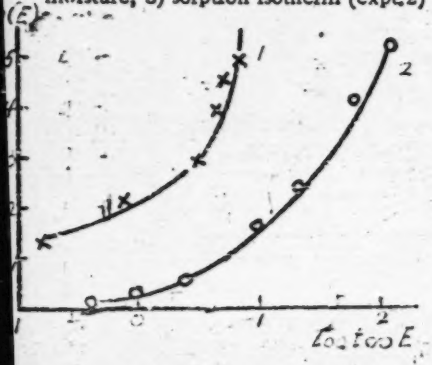

Fig. 8. Dependence of the activation energy distribution function for the sorption of oxygen on log t ∞ E: 1) $MgCr_2O_4$; 2) V_2O_5.

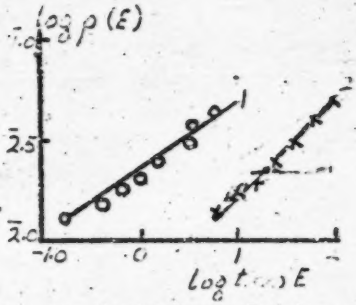

Fig. 9. Distribution function ρ(E) expressed in co-ordinates log ρ and log t: 1) for $MgCr_2O_4$; 2) for V_2O_5

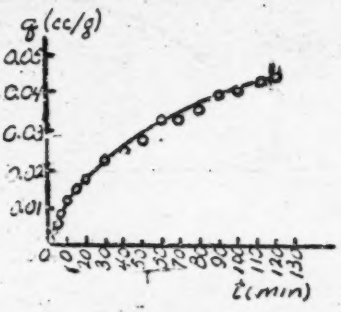

Fig. 10. Sorption isotherm for oxygen on V_2O_5 at 350° in presence of moisture.

Moisture was introduced into the catalyst in the following manner: A drop of water was frozen in the trap 41 by the aid of liquid nitrogen, the catalyst was carefully activated, and the water was then thawed and allowed to pass to the reaction vessel, where it was absorbed by the catalyst. Residual aqueous vapor was rapidly pumped off. The sorption isotherms for dehydrated V_2O_5 in presence of moisture are given in Fig. 4. The amount of sorbed oxygen at a given temperature is reduced in presence of moisture. Experiments were carried out on V_2O_5 (Fig. 10) which showed that presence of moisture in the catalyst reduces sorption of oxygen. This change in the sorption points to the blocking by the water of active sorption centers.

Thus, on passing from V_2O_5 to V_2O_4, we find a considerable increase in the sorption of oxygen at 350-450°. On the other hand, presence of moisture on the surface of the catalyst reduces both the amount of sorbed oxygen and the rate of sorption. The surfaces of vanadium catalysts and of magnesium chromite are heterogeneous with respect to the activation energy for the sorption of oxygen. The form of the distribution function for activation energies is the same for both types of catalyst. Consequently, both on V_2O_5, and also on magnesium chromite, there is an assembly of sites of varying activation energy for the sorption of oxygen, which participate in a varying manner in the catalytic oxidative process. Nevertheless, it is doubtful whether the heterogeneity of the surface with respect to activated sorption of oxygen can explain the differences in the course of the oxidation of hydrocarbons (mild and far-reaching reaction). Study of oxygen exchange on these catalysts ought to give an idea of the mobility of oxygen on the surface during the oxidation reaction.

2. Oxygen Exchange on Various Oxidation Catalysts

The results on oxygen exchange on vanadium pentoxide, on vanadium tetroxide, and on magnesia-chrome

catalyst are given in Tables 1 and 2. The O^{18} content in natural carbon dioxide is taken as the unit. If the coefficient for enrichment in $CO^{18}O^{16}$ is unity, then there is no exchange between the oxygen of the gas phase and the oxygen of the catalyst.

TABLE 2

Exchange between Oxygen in the Catalyst and Gaseous Oxygen

No.	Catalyst	Temp. °C	Enrichment coefficient $CO^{18}O^{16}/CO_2^{16}$		
			H_2O absent	H_2O present	CO_2^{16} present
1	V_2O_5 containing O^{18}	350	1.0	—	1.0
2	V_2O_4 containing O^{18}	350	1.13	1.22	1.10
3	$MgCr_2O_4$ containing O^{18}	350	1.0	—	1.0
4	Silver catalyst	270	1.05	—	—

Hence, in absence of moisture and in presence of the reaction product CO_2^{16} sorbed on the catalyst at 350°, oxygen exchange is not observed on V_2O_5 and on $MgCr_2O_4$. On V_2O_4 under the same conditions oxygen exchange proceeds to an insignificant extent, the enrichment coefficient $CO^{16}O^{18}/CO_2^{16}$ being 1.13 and 1.10. The presence of moisture increases the oxygen exchange, but only slightly.

As a result of the oxidation of hydrocarbons at the surface of the catalyst, moisture will always be present and oxygen exchange will consequently occur. From the oxygen exchange we may evaluate the extent of desorption of oxygen from the catalyst at the reaction temperature; as the results show, the extent to which desorption occurs is not great. In every oxidative process in presence of oxygen in the gas phase and on the surface of the catalyst, two reactions proceed simultaneously: 1) oxidation at the surface by the oxygen of the catalyst, 2) oxidation by oxygen from the gas phase.

The rates of these two reactions are different on mild-oxidation catalysts and on catalysts that promote far-reaching oxidation. It is probable that the mobility of oxygen during reaction is not the same as when hydrocarbon is absent. The specificity of oxidation catalysts cannot be explained by the degree of oxygen exchange at 350-450°. Only by a study of the kinetics of oxygen exchange on various catalysts will it be possible to establish the relation between the activity of oxidation catalysts and the extent of oxygen exchange.

SUMMARY

1. The kinetics of activated sorption of oxygen on vanadium catalysts at 250-400° have been studied.

2. It has been shown that the surface of vanadium catalysts is heterogeneous with respect to the activation energies of oxygen sorption.

3. A mass-spectrometric method of analysis has been applied to the study of oxygen exchange at catalysts containing heavy oxygen.

4. Oxygen exchange has been studied on catalysts of mild and far-reaching oxidative effect at the temperature of the oxidation reaction (350-450°).

Graduate T. V. Bykova took part in the work.

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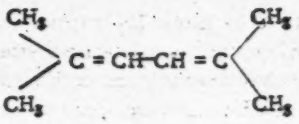
CATALYTIC HYDROGENATION OF DOUBLY UNSATURATED COMPOUNDS HAVING A CONJUGATED SYSTEM OF DOUBLE BONDS

COMMUNICATION 1. HYDROGENATION OF BIISOCROTYL

B. A. Kazansky and N. I. Popova

Lebedev [1] expressed the opinion that addition of hydrogen to conjugated dienes in presence of a catalyst (platinum black) may proceed in various ways, according to the structure of the diene, and he proposed that dienes should be divided accordingly into the following four types.

Type I. Hydrogenation of dienes of this type proceeds in strictly selective fashion in two stages. In the first stage addition of hydrogen occurs exclusively in the 1,4-positions of the conjugated system with formation of an ethylene compound having a double bond between atoms 2 and 3 of the original conjugated system, i.e. the first stage of hydrogen addition goes exclusively according to Thiele's rule. The curve representing this process should have a sharp break corresponding to the moment at which addition of the first hydrogen molecule is complete and should be reminiscent in form of the hydrogenation curve for a binary mixture of ethylenic compounds differing in degree of substitution, which will hydrogenate successively at different rates. Lebedev supposed that compounds of type I include compounds in which all four hydrogen atoms on the first and fourth carbon atoms of the conjugated system (1,3-butadiene) are replaced by aliphatic radicals. An example of such compounds is biisocrotyl (2,5-dimethyl-2,4-hexadiene):



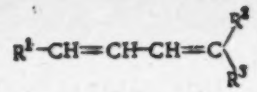
It must be remarked, however, that Lebedev, while ascribing biisocrotyl to the first type of dienes, brought forward no experimental data in support of this view and, in particular, gave neither a hydrogenation curve, nor an analysis of the reaction products.

Type II. In this case addition of hydrogen does not proceed in selective fashion, and the reaction proceeds in all possible directions, i.e. in the 1,2-, 3,4-, and 1,4-positions of the conjugated system; also, complete hydrogenation occurs. In this case the process does not go according to Thiele's scheme, and the reaction rate curves have a very complex form. For example, the curves for the hydrogenation of piperylene and 1,3-butadiene each have three distinct sections; the curve for isoprene has four. Also, addition of one molecule of hydrogen to a compound of this type is not accompanied by a change in the number of active components in the mixture undergoing hydrogenation. The kinetic curves for the reaction do not therefore show a break at this point; the break occurs considerably later — when 65-70% of the amount of hydrogen required for complete saturation of the system has been added — and corresponds to the disappearance of the initial conjugated diene. Lebedev called this point "the critical point for hydrogenation of the conjugated system". All substances whose hydrogenation was studied by Lebedev belong to type II, i.e. 1,3-butadiene, isoprene, piperylene, 2,3-dimethyl-1,3-butadiene, and others.

Type III. Lebedev referred to this type as being theoretically possible, but never observed in any of his experiments. In this case the hydrogen must add all at once to the extent of two molecules to give the saturated compound. During the whole hydrogenation process the reaction products must consist of a mixture of the fully hydrogenated substance and the original diene in various proportions. Hydrogenation curves for substances of type III will not have breaks, but will be reminiscent of the hydrogenation curves of individual mono-olefins.

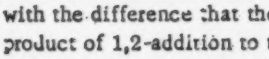
Type IV. 1,4-Addition of hydrogen to the conjugated system in compounds of this type does not take place at all. The separate double bonds are hydrogenated on their own and independently, as in non-conjugated diene systems. Within this type Lebedev supposed two subtypes to be possible.

Type IVA. The double bonds differ in degree of substitution:



In this case they are saturated by hydrogen at differing rates, and the hydrogenation curve will show a break at the point for the addition of one molecule of hydrogen. In general, the curve for this type is reminiscent in form of that for type I, with the difference that the mono-olefin formed in this case by addition of one molecule of hydrogen will be a product of 1,2-addition to the conjugated system. It should be noted that there is not a single example in Lebedev's work of a substance that undergoes hydrogenation according to type IVA.

Type IVB. In this case the double bonds are identical in degree of substitution:



The two double bonds will hydrogenate simultaneously, and the hydrogenation curve will be reminiscent in form of that for a mixture of mono-olefins that are homogeneous with respect to degree of substitution. If the hydrogenation process is interrupted when the addition of one molecular proportion of hydrogen has occurred, the hydrogenation product will consist of a mixture of the original diene, mono-olefins (1,2 and 3,4 hydrogen addition products), and the fully saturated substance. Products of the 1,4-addition of hydrogen to the conjugated system will be absent among the products of incomplete hydrogenation. It is possible to regard 2,4-hexadiene as an example of this type; in fact, the hydrogenation curve for 2,4-hexadiene in presence of platinum black has, according to Lebedev, a break at the point corresponding to addition of 70% of hydrogen, but Lebedev does not give the analysis of reaction products that is necessary so that 2,4-hexadiene may be with certainty ascribed to type II or to type IVB. Thus, as already stated above, all the substances investigated by Lebedev must be ascribed to type II in the scheme of classification that he has proposed, for the addition to them of hydrogen in presence of platinum proceeds in all possible directions.

The statements by Vavon and coworkers [2] and by Ingold [3] that in the catalytic hydrogenation of compounds having conjugated double bonds it is possible for the conjugated system to become completely saturated in one step with formation of a mixture of the fully saturated compound and the non-hydrogenated compound (without intermediate formation of mono-olefins) have not been confirmed and were evidently the results of defects in the procedure used for the investigation of the reaction products. The observation of Paal [4], that in presence of colloidal palladium piperic acid goes direct to tetrahydropiperic acid, was not confirmed by Lebedev [5], who showed that both in presence and in absence of platinum black piperic acid is hydrogenated according to type II. The more recent work of Farmer and Galley [6] has shown that in the partial hydrogenation of doubly unsaturated acids having a conjugated system of double bonds hydrogen adds in several ways simultaneously, i.e. according to Lebedev's type II. The reaction products were analyzed by the aid of oxidation and ozonization reactions. It was shown also by Farmer and Hughes [7] that the course of the hydrogenation of these compounds depends on the nature of the catalyst and of the solvent. The ratio of reaction products varies somewhat with different catalysts; variation of the solvent affects only the rate of hydrogenation, and not the manner in which hydrogen addition occurs. In the experiments of Farmer and Hughes, palladium always showed a selectivity greater than that of platinum or of nickel.

Dupont and co-workers [8] studied the hydrogenation of isoprene and 2,3-dimethyl-1,3-butadiene in presence of Raney nickel. Analysis of the products of the hydrogenation of these hydrocarbons, with the aid of their Raman spectra, showed that addition of half of the total hydrogen equivalent to each of these leads to the formation both of olefins having the double bond in the 1,2-position and also of olefins having a 2,3-double-bond.

Young and co-workers [9] showed that butadiene, in full agreement with Lebedev's results, hydrogenates according to type II in presence of one of the following four catalysts: platinum (from the oxide), palladium (from the oxide), palladium (deposited on barium sulfate), and Raney nickel. The lower selectivity of hydrogenation in presence of platinum, as compared with palladium, was observed also by Young. Also, Young showed that in the hydrogenation process it is possible for the double bond in a mono-olefin to undergo migration; thus in the hydrogenation of 2-butene to an extent of about 20% in presence of the catalysts $Pd/BaSO_4$, it was found that the unhydrogenated residue consisted of 8% and 92% 2-butene. In the 50% hydrogenation of 2-butene, isomerization again occurred; the composition of the butene residue was 8.5% 1-butene, 20.5% cis-2-butene, and 71% trans-2-butene. If such double-bond migration is a general phenomenon in the hydrogenation process for dienes, then it is impossible to form any opinion of the mechanism of the hydrogenation of dienes or to discover any regularities in this reaction that are related to the structure of the original substance.

This review of work on the catalytic hydrogenation of compounds having a conjugated system of double bonds shows that practically all such compounds are hydrogenated in a non-selective fashion, i.e. according to Lebedev's type II. Selectivity is to be observed in hydrogenation only when certain groups are present in the molecule (e.g. phenyl groups). Thus Kazansky and Tatevosyan [10] observed that both in the presence of platinum black, and also in presence of palladium black diphenylfulvene is hydrogenated selectively: the first two hydrogen molecules add at the two double bonds of the five-membered ring, and only then does addition of hydrogen at the remaining fulvene double bond begin. At the same time, dimethylfulvene, which has a structure similar to that of diphenylfulvene, does not show the same sharply defined selectivity when hydrogenated; this selectivity is evidently associated with the aromatic nature of the substituents on the extranuclear carbon atom.

The Lebedev types I, IVA, and IVB have remained without study from the experimental point of view. Hence, in 1940, Kazansky and Mikheev [11] subjected biisocrotyl, which belongs to type I, to catalytic hydrogenation in presence of platinum black. It was found that the hydrogenation curve for biisocrotyl did indeed show an inflection corresponding to the addition of one molecule of hydrogen; this gave some basis for the supposition that the process is selective and that, since the double bond system of biisocrotyl is of a symmetric nature, addition of hydrogen occurs primarily in the 1,4-positions. However, it was not found possible in 1940 to study the products of the addition of one molecule of hydrogen to biisocrotyl in detail, and the question of the order of this addition remained an open one.

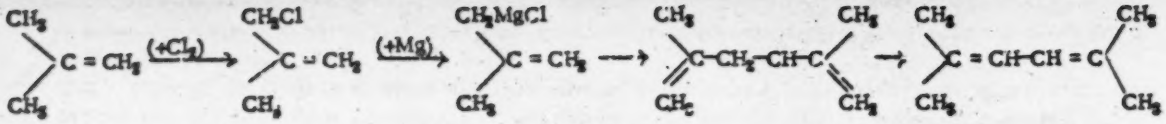
In the present work we have been able to make a more detailed investigation of this reaction, for we have had a much greater amount of biisocrotyl at our disposal and have been able to submit the hydrogenation products to precise fractionation. Also, the properties of 2,5-dimethyl-3-hexene, the product of the addition of one molecule of hydrogen to biisocrotyl at the 1,4-positions, were previously to be found only in Egloff's reference book [12], where reference is made to unpublished work without any indication of the method by which the hydrocarbon was prepared; only in 1950 was the synthesis of this hydrocarbon described [13]. Thus, only very recently has it become possible to carry out a chemical investigation into the products of the catalytic hydrogenation of biisocrotyl with sufficient confidence. The results of this investigation show that in presence of platinum black, of palladium black, or of Raney nickel the curves for the hydrogenation of biisocrotyl show a clearly defined break at the point corresponding to the addition of one molecule of hydrogen; this break is most clearly marked on the curve for hydrogenation in presence of palladium.

Nevertheless, in spite of this indication of the selectivity of the process, a detailed investigation into the composition and nature of the reaction products shows that in all cases the process proceeds non-selectively, i.e. in all possible directions, addition at the 1,2-positions of the conjugated system being, however, the most favored reaction (in all cases 2,5-dimethyl-2-hexene is the main reaction product). In the example we have taken there is a complete analogy, with respect to order of addition, between hydrogenation with catalytically activated hydrogen, that with hydrogen at the moment of its formation, and that with hydrogen that is adding under the influence of the sodium-liquid ammonia system [15]. It is evident that the order of addition of hydrogen to biisocrotyl is determined more by the structure of the molecule undergoing hydrogenation than by the nature of the hydrogen or of the catalyst. The effect of the latter is to be seen in the extent to which the saturated hydrocarbon is formed; it is less for palladium black, and particularly for Raney nickel, than for platinum. In this sense, hydrogenation of biisocrotyl proceeds in a less selective fashion on the last catalyst. Also, as will be seen later, the ratio between the amounts of hydrogen giving 1,2- and 1,4-addition, i.e. between the amounts of 2,5-dimethyl-2-hexene and of 2,5-dimethyl-3-hexene, also varies according to the nature of the catalyst. As regards migration of the double bond during catalytic addition of hydrogen to the diene, as found by Young in his work [9] (see above), in the case of the hydrogenation of biisocrotyl this phenomenon was not observed; this was proved by direct experiments on the partial hydrogenation of 2,5-dimethyl-2-hexene, when formation of 2,5-dimethyl-3-hexene, b.p. 102° was not detected; the first to distil off was 2,5-dimethylhexane, which has a considerably higher boiling point.

EXPERIMENTAL

1. The Synthesis of Biisocrotyl. Biisocrotyl was synthesized as indicated in the following scheme: (see top of next page)

Isobutene was chlorinated in the gas phase at room temperature [16]. The methylallyl chloride so obtained had b.p. 70-71° at 740 mm; n_D^{20} 1.4277; d_4^{20} 0.9258. By the action on this of metallic magnesium in absolute ether, 2,5-dimethyl-1,5-hexadiene was obtained in 84% yield; b.p. 113.7-114.0° at 758 mm; n_D^{20} 1.4296; d_4^{20} 0.7428; found MR_D 38.30; calculated for C_8H_{14} MR_D 38.21.



2,5-Dimethyl-1,5-hexadiene was isomerized in presence of aluminium oxide at 225-230° into 2,5-dimethyl-2,4-hexadiene (biisocrotyl) [17]. By distillation of the catalyzate through a column of 40 theoretical plates, biisocrotyl (262.5 g) was isolated; it had the following constants: b.p. 134.2-134.5° at 750 mm; m.p. 14.6-14.8°; n_D^{20} 1.4780; d_4^{20} 0.7635; found MR_D 40.86; calculated C_8H_{14}, MR_D 38.21; increment of MR_D 2.65. [18]: b.p. 134.5° at 760 mm; m.p. 13.94°; n_D^{20} 1.4781; d_4^{20} 0.7615; found MR_D 40.97; calculated C_8H_{14}, MR_D 38.21, increment of MR_D 2.76.

2. Method of Hydrogenation and of Investigation of the Composition of the Reaction Products. Hydrogenation was carried out by Lebedev's method at ordinary temperature and pressure in a flask shaken at a rate of not less than 300 complete oscillations per min. The rate of hydrogen absorption was measured accurately by the aid of gas burets graduated in 0.2 mm divisions, readings being taken every 0.5 min. Platinum black and palladium black were prepared by Willstatter's method [19], and nickel was prepared from nickel-aluminum alloy by Adkins' method [20]. Each series of experiments was carried out with different portions of the same sample of catalyst; 96% alcohol was always used as solvent.

The addition products from one molecule of hydrogen and one of biisocrotyl were distilled off together with the alcohol from a Favorsky flask, the catalyst being first filtered off; their azeotropic mixtures with alcohol boil between 71 and 73° approximately. The alcohol present in the distillate was extracted by means of calcium chloride solution, and the mixture of hydrocarbons separated in this way was fractionated in a column designed for accurate rectification. The distillation curve indicated which hydrocarbons were present in the mixture; their identification and quantitative estimation in the fractions were based on the boiling points, densities, refractive indices, and bromine numbers of the fractions. From all these data it was possible to draw up a complete balance sheet for the hydrogenation reaction with the given catalyst.

3. Hydrogenation of Biisocrotyl in presence of Platinum Black. Two experiments were carried out with small amounts in order to obtain kinetic curves for the hydrogenation. The results are given in Table 1.

TABLE 1

Expt. No.	Amt. of hydrocarbon (g)	Amt. of catalyst (g)	Amt. of alcohol (ml)	Pressure (mm Hg)	Temp. °C	Vol. of hydrogen (ml) calculated	Vol. of hydrogen (ml) absorbed
1	0.3130	0.050	20	750	23	145.3	145.2
2	0.2994	0.086	20	750	18	134.2	135.3

The course of hydrogenation in expt. 2 is shown by the curve in Fig. 1. It will be seen from this curve that the first molecule of hydrogen adds at a fairly constant rate; the rate of hydrogenation then falls and is gradually reduced to a very low value. In expt. 1 hydrogenation proceeded in similar fashion, but at a lower rate. In order to make a detailed investigation of the composition of the products of the hydrogenation of biisocrotyl at the stage corresponding to addition of one molecule of hydrogen, two experiments were carried out. In each of

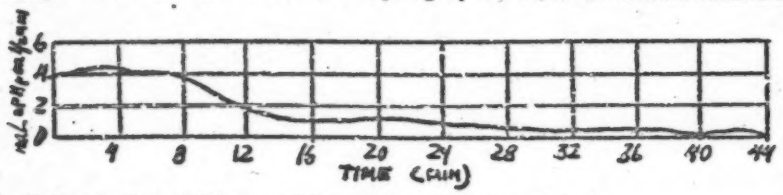


Fig. 1. Hydrogenation of biisocrotyl in presence of platinum black

these biisocrotyl (13 g) was dissolved in alcohol (100 ml), and platinum black (1 g) was added to the solution. When the hydrogenation reaction was complete, the mixture of hydrocarbons was washed free from alcohol and distilled through a column of 30 theoretical plates; the amount of the mixture taken for distillation was 22.45 g

(30.5 ml). The distillation curve is given in Fig.2.

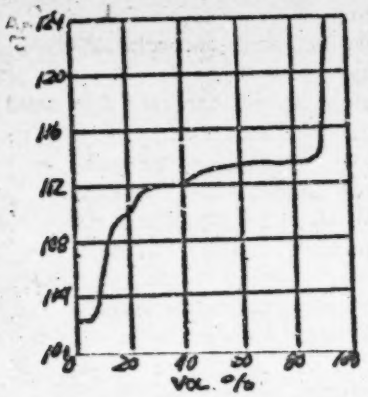


Fig.2. Distillation curve for the product of addition of one molecule of hydrogen to biisocrotyl in presence of platinum.

For each fraction collected determinations were made of refractive index, density, and bromine number (by Galpern and Vinogradova's modification [21] of Kaufmann's method). The results of all these determinations are given in Table 2. The bromine number of the pure mono-olefins (octenes) is 142.5.

The physical constants of the hydrocarbons that could be formed by partial and complete hydrogenation of biisocrotyl are given in Table 3.

From a consideration of the properties, including the bromine numbers, of the fractions obtained by distillation and from a consideration of the properties of the hydrocarbons given in Table 3, it is possible to calculate the composition of the mixture obtained by addition of one molecule of hydrogen to biisocrotyl:

2,5-Dimethyl-3-hexene 13%
2,5-Dimethyl-2-hexene 69%
2,5-Dimethylhexane 13%
Biisocrotyl 11%

TABLE 2

Fraction No.	B.p. (°C)	Pressure, (mm Hg)	n_D^{20}	d_4^{20}	Bromine No.	Olefin content of fraction %	Amt. of fraction, wt. %	Amt. of olefins, wt. %
1	102.1	760	1.4038	0.6990	143.1	100.4	6	6
2	102.1-109.8	760	1.4005	0.6778	90.5	63.5	11	7
3	109.8-109.9	760	1.4030	0.7037	84.3	59.2	3	2
4	109.9-112.0	760	1.4075	0.7084	95.6	67.1	18	12
5	112.0-113.2	760	1.4126	0.7146	126.6	88.8	15	13
6	113.2-113.3	760	1.4150	0.7132	143.8	100.9	32	32
7	113.3-126.5	760	1.4401	—	—	—	4	2
Residue in flask	—	—	1.4720	—	—	—	—	—
Residue in column	—	—	—	—	—	—	9	—
Losses	—	—	—	—	—	—	—	—

In the calculation it was assumed that fractions 1 and 2 contain 2,5-dimethylhexane and, of the olefins, 2,5-dimethyl-3-hexene; that fractions 3,4,5, and 6 contain 2,5-dimethylhexane and, of the olefins, 2,5-dimethyl-2-hexene; that fraction 7 consists of 50% 2,5-dimethyl-2-hexene and 50% biisocrotyl; and that the residue in the column consists entirely of biisocrotyl.

4. Hydrogenation of Biisocrotyl in presence of Palladium Black. Three experiments were carried out with different amounts of palladium black on the hydrogenation of biisocrotyl. The conditions of the experiments are shown in Table 4. The hydrogenation curve for expt. 3 is given in Fig. 3. It is similar in outward appearance to the curve for hydrogenation of biisocrotyl in presence of platinum, but the break corresponding to addition of one molecule of hydrogen is more marked. The character of the curve does not change with change in the amount of catalyst.

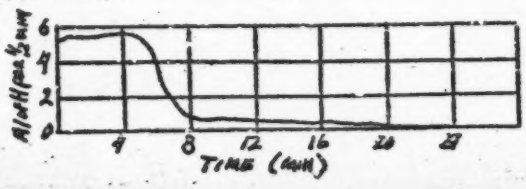


Fig. 3. Hydrogenation of biisocrotyl in presence of palladium black.

TABLE 3

Hydrocarbon	B.p. °C at 700 mm Hg	n_D^{20}	d_4^{20}	Literature Reference
2,5-Dimethyl-3-hexene	102.0-102.1	1.4030	0.7124	[12]
	123.5 (755 mm)	1.4100	0.7122	[13]
2,5-Dimethyl-2-hexene	112.0	1.4144	0.7190	[12]
2,5-Dimethylhexane	109.1	1.3925	0.6936	[22]

In order to make a detailed study of the products arising from the addition of one molecule of hydrogen to biisocrotyl, 75.45 g of this hydrocarbon was hydrogenated in several portions; for 10 g, 0.5-0.7 g of palladium black and 100-150 ml of alcohol were taken. According to calculation, for addition of one molecule of hydrogen to biisocrotyl under the conditions of the experiments 17.5 ml of hydrogen would be required. 18.4 ml was added, i.e. 1.04 mole of hydrogen. When the catalyst had been filtered off from the alcoholic solution, the latter was treated as previously described. The separated mixture of hydrocarbons was distilled through a column of 40 theoretical plates; 68 g (93.5 ml) of the mixture was taken for the distillation. The distillation curve is given in Fig. 4, and the properties of the fractions are given in Table 5.

TABLE 4

Expt. No.	Amt. of hydrocarbon(g)	Amt. of catalyst(g)	Amt. of alcohol(ml)	Pressure (mm Hg)	Temp. °C	Vol. of hydrogen(ml) calculated	absorbed
1	0.2980	0.05	20	745	23	137.2	136.9
2	0.3135	0.10	20	745	23	145.5	146.5
3	0.2710	0.06	20	745	23	126.4	126.5

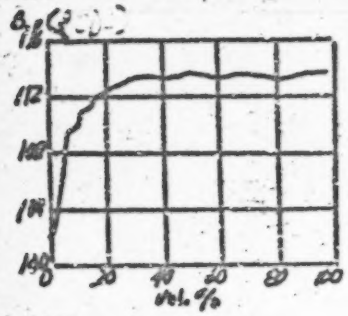


Fig. 4. Distillation curve for the product of addition of one molecule of hydrogen to biisocrotyl in presence of palladium.

A simple examination of the distillation curve for the mixture of hydrocarbons formed as a result of addition of one molecule of hydrogen to biisocrotyl in presence of palladium black indicates that 2,5-dimethyl-2-hexene, b.p. 112°, predominates in this mixture to an appreciable extent. Calculation on the basis of data in Table 5 of the composition of the mixture yields the result:

2,5-Dimethyl-3-hexene . . . 6%
2,5-Dimethyl-2-hexene . . . 86%
2,5-Dimethylhexane 7%

5. Hydrogenation of Biisocrotyl in presence of a Raney Nickel Catalyst. Three experiments with Raney nickel catalyst were carried out under the conditions shown in Table 6.

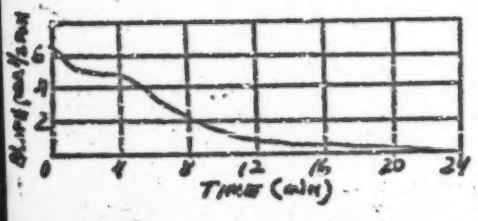


Fig. 5. Hydrogenation of biisocrotyl in presence of a Raney nickel catalyst.

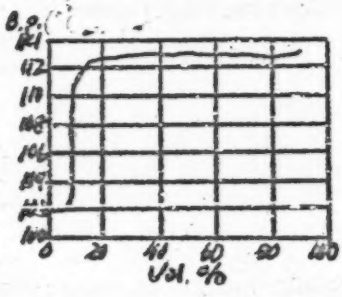


Fig. 6. Distillation curve for the product of addition of one molecule of hydrogen to biisocrotyl in presence of nickel.

TABLE 5

Fraction No.	B.p. (°C)	Pressure, (mm Hg)	n_D^{20}	d_4^{20}	Bromine No.	Olefin content of fraction, %	Amt. of fraction, wt. %	Amt. of olefins, wt. %
1	102.2	760	1.4038	0.6990	144.8	101.7	2	2
2	102.0-109.7	760	1.3979	0.6972	73.6	51.7	8	4
3	109.7-112.7	760	1.4078	0.7115	109.0	76.5	15	12
4	112.7-113.2	760	1.4128	0.7168	145.6	102.2	16	16
5	113.2	760	1.4157	0.7183	145.4	162.2	55	55
Residue	–	–	1.4190	–	–	–	2	2
Losses	–	–	–	–	–	–	2	–

TABLE 6

Expt. No.	Amt. of hydrocarbon(g)	Amt. of catalyst(g)	Amt. of alcohol(ml)	Pressure(mm Hg)	Temp. °C	Vol. of hydrogen(ml)	
						calculated	absorbed
1	0.3310	0.2	25	750	27	155.5	Hydrogenation not carried out to completion
2	0.3072	0.1	20	750	27	144.2	
3	0.2666	0.1	20	745	23	123.7	

TABLE 7

Fraction No.	b.p. (°C)	Pressure, (mm Hg)	n_D^{20}	d_4^{20}	Bromine No.	Olefin content of fraction, %	Amt. of fraction, wt. %	Amt. of olefins, wt. %
1	102.0	760	1.4045	0.6988	144.5	101.4	6	6
2	102.0-112.2	760	1.4044	0.7062	134.6	94.5	7	6
3	112.2-113.1	760	1.4143	0.7164	145.5	102.1	13	13
4	113.1-113.2	760	1.4157	0.7183	145.2	101.9	62	62
Residue in flask	–	–	1.4222	–	–	–	11	11
Residue in column	–	–	–	–	–	–	–	–
Losses	–	–	–	–	–	–	1	–

In Fig.5 we give the hydrogenation curve for expt. 2; the hydrogenation curves obtained in the other experiments were similar to this in character. They are all distinguished by the gentle character of the slope, as compared with the curves obtained in experiments with platinum and palladium; the break corresponding to addition of one molecule of hydrogen is not so marked, and the second molecule of hydrogen adds more and more slowly, so that it is rather difficult to cause hydrogenation to go to completion. When a large amount of catalyst is used (expt. 1), the curve has a short horizontal part and shows a rapid fall.

In order to make a study of the hydrogenation products, one molecular proportion of hydrogen was added to biisocrotyl (51 g). The mixture of hydrocarbons obtained after preparatory treatment as before was distilled through a column of 50 theoretical plates; altogether 48 g (66 ml) was distilled. The results of the distillation are shown in the curve of Fig.6 and in Table 7.

In the mixture formed by hydrogenation of biisocrotyl, 2,5-dimethyl-2-hexene predominates to an extent that is even greater than in the experiments with platinum and palladium.

In the calculation of the amounts of the separate hydrocarbons formed in the addition of one molecular proportion of hydrogen to biisocrotyl in presence of nickel, it was assumed that fraction 1 and 50% of fraction 2 consisted of 2,5-dimethyl-3-hexene and that fractions 3 and 4, 50% of fraction 2, and the residues in the flask

and in the column consisted of 2,5-dimethyl-2-hexene. Fraction 2 contains also 2,5-dimethylhexane. The calculation gave the following result:

2,5-Dimethyl-3-hexene . . . 9%
2,5-Dimethyl-2-hexene . . . 90%
2,5-Dimethylhexane 1%

6. Experiments on the Isomerization of 2,5-Dimethyl-2-hexene. In order to find out whether 2,5-dimethyl-3-hexene is formed in our experiments as a result of secondary isomerization of 2,5-dimethyl-2-hexene in presence of catalyst and hydrogen, just as 1-butene in the experiments of Young and collaborators [9] underwent isomerization during its partial hydrogenation into 2-butene, we tried the addition to 2,5-dimethyl-2-hexene of 20-25% of the hydrogen necessary for saturation in presence of platinum black and of Raney nickel. Partial isomerization would have been readily observed since the 2,5-dimethyl-3-hexene that would be formed boils at 102°, i.e. 7° lower than 2,5-dimethylhexane and 10° lower than 3,5-dimethyl-2-hexene. The following results were obtained:

To 2,5-dimethyl-2-hexene (19 g), b.p. 112.5-113° at 755 mm; n_D^{20} 1.4153 and d_4^{20} 0.7182, isolated in the course of the partial hydrogenation of diisooctyl in the previous experiments, 25% of the hydrogen required for complete saturation was added in presence of platinum black. The catalyzate was treated in the usual way and then distilled through a column of 40 theoretical plates. The first fraction boiled at 108° at 740 mm and had n_D^{20} 1.3950, i.e. was 2,5-dimethylhexane.

To 2,5-dimethyl-2-hexene (18.3 g) with the above-indicated properties 20% of the hydrogen necessary for complete saturation was added in presence of a Raney catalyst. In the distillation of the catalyzate through the same column, the first fraction boiled at 109.5° at 750 mm and had n_D^{20} 1.3950.

Thus, movement of the double bond to the center of the molecule with formation of 2,5-dimethyl-3-hexene did not occur either with a platinum or with a Raney nickel catalyst.

SUMMARY

1. Diisooctyl, which, according to Lebedev, should be ascribed to type I in his proposed scheme for the classification of dienes, is hydrogenated in presence of platinum, palladium, and nickel in all possible ways, and must be ascribed therefore to type II.

2. In presence of each of these catalysts, 1,2-addition predominates.

3. The lowest selectivity in the addition of hydrogen is observed in presence of platinum, and the greatest in presence of nickel, when 90% of the hydrogenation product consists of 2,5-dimethyl-2-hexene (1,2-addition of hydrogen) and there is practically no formation of alkane.

4. In no case does the form of the curve for the rate of hydrogen addition indicate the characteristics of the actual course of reaction.

5. When 2,5-dimethyl-2-hexene is hydrogenated in presence of platinum or nickel, transposition of the double bond to the center of the molecule is not observed.

6. Variation in the amount of catalyst has no effect on the character of the hydrogenation curve.

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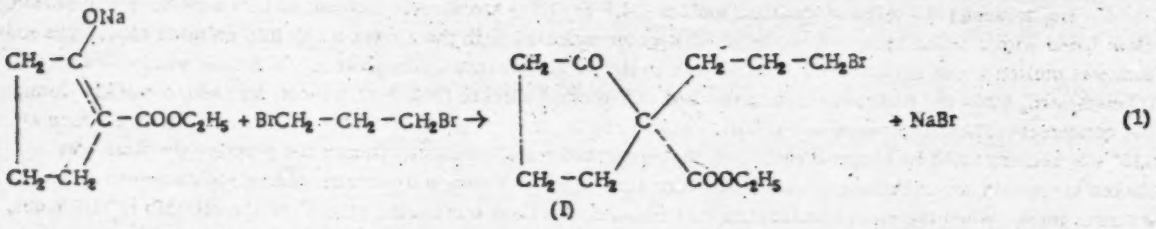
THE PREPARATION OF THE ETHYL ESTERS OF 1-(3-BROMOPROPYL)-2-OXOCYCLOPENTANECARBOXYLIC ACID AND OF 1-(3-CHLOROPROPYL)-2-OXOCYCLOPENTANECARBOXYLIC ACID

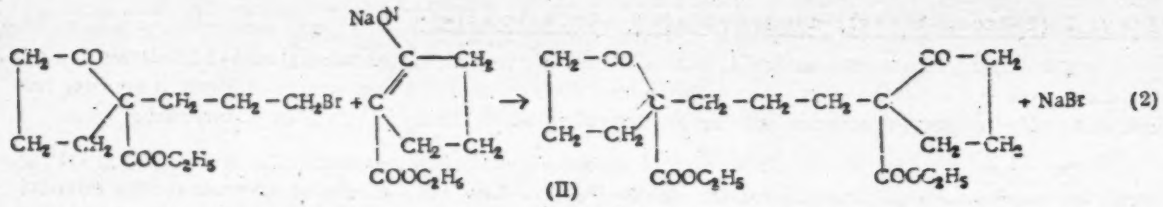
N.D.Zelinsky and N.V.Elagina

In order to prepare the ethyl ester of 1-(3-bromopropyl)-2-oxocyclopentanecarboxylic acid (I), which we required for our work, we carried out the reaction of 1,3-dibromopropane with the sodium derivative of the ethyl ester of 2-oxocyclopentanecarboxylic acid:



(1)

We found that, when the reaction is carried out with equimolecular amounts of the reactants at room temperature, the yield of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate (I) is only about 20% of the theoretical. The low yield of (I) may be explained on the assumption that it reacts, as it is formed, with the sodium derivative of ethyl 2-oxocyclopentanecarboxylate with formation of the ester of a dicarboxylic acid (II):



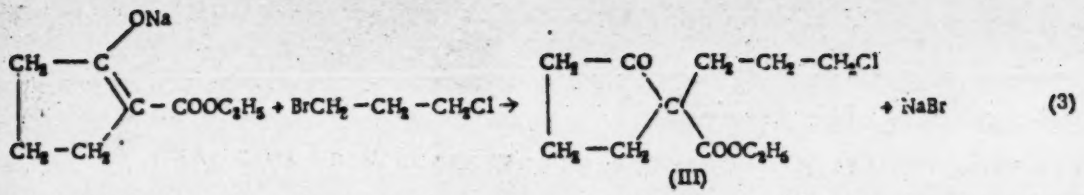
(2)

Also, it is possible under the conditions of the experiment for the ester of 2-oxocyclopentanecarboxylic acid to be converted by the action of sodium ethoxide into the ester of adipic acid.

In an effort to raise the yield of the ester in which we were interested, we carried out the reaction between the sodium derivative of ethyl 2-oxocyclopentanecarboxylate and 1,3-dibromopropane using the latter in quantity $1\frac{1}{2}$ times that required by Equation (1). In order to avoid the splitting effect of sodium ethoxide on the oxocyclopentanecarboxylic ester, we took a somewhat smaller amount of sodium for the reaction than that required by theory, and we applied external cooling down to −15°. In this experiment the yield of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate was 32.2% of the theoretical.

In an experiment carried out with three times the theoretical amount of 1,3-dibromopropane, the yield of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate was raised to 46.3%. Four times the theoretical amount of the dibromopropane gave a 52.4% yield of the required ester. Thus, increase of the concentration of 1,3-dibromopropane in the reaction mixture inhibits Reaction 2 between ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate and the sodium derivative of ethyl 2-oxocyclopentanecarboxylate and leads to increase in the yield of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate.

Ethyl 1-(3-chloropropyl)-2-oxocyclopentanecarboxylate (III) was obtained by us by the action of 1-bromo-3-chloropropane on the sodium derivative of ethyl 2-oxocyclopentanecarboxylate:



(III)

(3)

The yield of (III) in an experiment carried out with equimolecular amounts of the oxocyclopentanecarboxylic ester and the bromochloropropane was 67.8% of the theoretical.

The difference in the yields of the 1-(3-chloropropyl)- and the 1-(3-bromopropyl)-2-oxocyclopentanecarboxylic esters must be explained by the difference in reactivity of these compounds. The chloro derivative (III), owing to its lower reactivity in comparison with the bromo derivative (I), is less inclined to enter into reaction with the sodium derivative of the oxocyclopentanecarboxylic ester. The yield of ester (III) is therefore the greater.

EXPERIMENTAL

Ethyl 2-Oxocyclopentanecarboxylate

Dry toluene (600 ml) and metallic sodium (34.5 g; 1.5 g-atom) were introduced into a 2-liter round-bottomed flask fitted with a reflux spherical condenser that communicated with the air via a calcium chloride tube. The sodium was melted under the toluene and converted in the usual way into a fine powder. The flask was heated on an oil-bath, and, when the bath temperature reached 60°, diethyl adipate (303 g; 1.5 mole) was added quickly through the condenser. The temperature of the bath was allowed to rise slowly, and at 80° reaction commenced, which at 110° was accompanied by vigorous ebullition that continued for 15 minutes. During the reaction the flask was shaken vigorously several times. The sodium derivative of ethyl 2-oxocyclopentanecarboxylate came out as a voluminous mass. When the energetic reaction had finished, the flask was heated at 130° on the oil-bath for 1.5 hours.

The reaction mixture was cooled with ice and was decomposed with 10% acetic acid. The toluene layer was separated, and the aqueous layer was extracted with toluene. The united toluene solutions were washed with water, with a 7% solution of sodium carbonate, and again with water. The toluene was driven off, and the residue was vacuum-fractionated. The product was ethyl 2-oxocyclopentanecarboxylate (176.3 g; 75.3%), b.p. 83-84° at 5 mm.

Ethyl 1-(3-Bromopropyl)-2-oxocyclopentanecarboxylate (I)

The reaction between the sodium derivative of ethyl 2-oxocyclopentanecarboxylate and 1,3-dibromopropane was carried out in a 500-ml three-necked round-bottomed flask fitted with a mercury-sealed stirrer, a dropping funnel, and a reflux condenser protected from the moisture of the air by means of a calcium chloride tube.

Experiment 1. Absolute ethanol (80 ml) was introduced into the flask, and metallic sodium (4.4 g; 0.19 g-atom) was added gradually. When the sodium had dissolved, the flask was placed in an ice–salt cooling mixture, the temperature of which was maintained at about −15° throughout the reaction. Stirring was begun, and well-cooled ethyl 2-oxocyclopentanecarboxylate (31.2 g; 0.2 mole) was added slowly from a dropping funnel. When one-third of the total amount of ester had been added, its sodium derivative began to come out in white curds. The addition of the oxocyclopentane–carboxylic ester occupied 1 hour, and the mixture was then stirred for a further 1.5 hours. Strongly cooled 1,3-dibromopropane (60.5 g; 0.3 mole) was then rapidly introduced into the flask from the dropping funnel. When this addition was completed, stirring was continued for 1 hour with external cooling down to −15°. The mixture was then left overnight at room temperature. On the next day the reaction mixture, which had an alkaline reaction, was heated on a water bath maintained at 55-60°. The mixture was stirred for 5 hours, when a test made with moist litmus indicated a neutral reaction.

The reaction mixture, which was cooled with ice, was poured into ice water (400 ml), and the heavy light-yellow oil that settled on the bottom was separated. The aqueous layer was extracted with ether, and the ether extract was united with the oil already separated. The ethereal solution was washed with water and dried by means of anhydrous sodium sulfate. The ether was driven off, and the residue was vacuum-fractionated. Ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate (17.1 g; 32.2% yield based on the sodium taken for reaction), b.p. 164-166° at 8 mm, was obtained as a result of repeated fractionation.

Experiment 2. Ethyl 2-oxocyclopentanecarboxylate (31.2 g; 0.2 mole), metallic sodium (4.3 g; 0.187 g-atom), and 1,3-dibromopropane (121.1 g; 0.6 mole) were taken for reaction, the experiment being carried out under the conditions used in the first experiment. After repeated vacuum-fractionation of the reaction products, ethyl

1-(3-bromopropyl)-2-oxocyclopentanecarboxylate (24.0 g; 46.3% based on sodium taken), b.p. 164-166° at 8 mm, was obtained.

Experiment 3. Ethyl 2-oxocyclopentanecarboxylate (31.2 g; 0.2 mole), sodium (4.4. g; 0.19 g-atom), and 1,3-dibromopropane (161.5 g; 0.8 mole) were caused to react under the same conditions as before. Vacuum-fractionation of the products yielded ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate (27.8 g; 52.4% based on sodium taken), b.p. 164-166° at 8 mm.

Pure ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate had the following constants: b.p. 134-135° at 2 mm; n_D^{23} 1.4915; d_4^{20} 1.3178; found MR_D 60.97; calculated $C_{11}H_{17}O_3Br$ MR_D 60.23.

Found %: C 47.63; 47.78; H 6.31; 6.31; Br 28.59; 28.77
$C_{11}H_{17}O_3Br$. Calculated %: C 47.66; H 6.18; Br 28.83;

Ethyl 1-(3-Chloropropyl)-2-oxocyclopentanecarboxylate (III)

The experiment was carried out in the apparatus described for the synthesis of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate. Ethyl 2-oxocyclopentanecarboxylate (78.0 g; 0.5 mole) and 1-bromo-3-chloropropane (78.7 g; 0.5 mole) were taken for reaction. A solution of sodium ethoxide was prepared by the dissolution of metallic sodium (10.7 g; 0.47 g-atom) in absolute ethanol (200 ml). The experimental procedure was the same as that used in the preparation of ethyl 1-(3-bromopropyl)-2-oxocyclopentanecarboxylate. The reaction products were vacuum-fractionated. Ethyl 1-(3-chloropropyl)-2-oxocyclopentanecarboxylate (73.4 g; 67.8% on basis of sodium taken), b.p. 122-124° at 2 mm, was obtained.

Pure ethyl 1-(3-chloropropyl)-2-oxocyclopentanecarboxylate had the following constants: b.p. 134.5-135.5° at 4 mm; n_D^{20} 1.4718; d_4^{20} 1.1329; found MR_D 57.50; calculated $C_{11}H_{17}O_3Cl$ MR_D 57.33.

Found %: C 56.62; 56.62; H 7.35; 7.46; Cl 14.84; 14.86;
$C_{11}H_{17}O_3Cl$. Calculated %: C 56.77; H 7.36; Cl 15.24.

SUMMARY

1. A study has been made of the reactions of the sodium derivative of ethyl 2-oxocyclopentanecarboxylate with 1,3-dibromopropane and with 1-bromo-3-chloropropane.

2. The ethyl esters of 1-(3-bromopropyl)-2-oxocyclopentane-carboxylic acid and of 1-(3-chloropropyl)-2-oxocyclopentanecarboxylic acid have been prepared.

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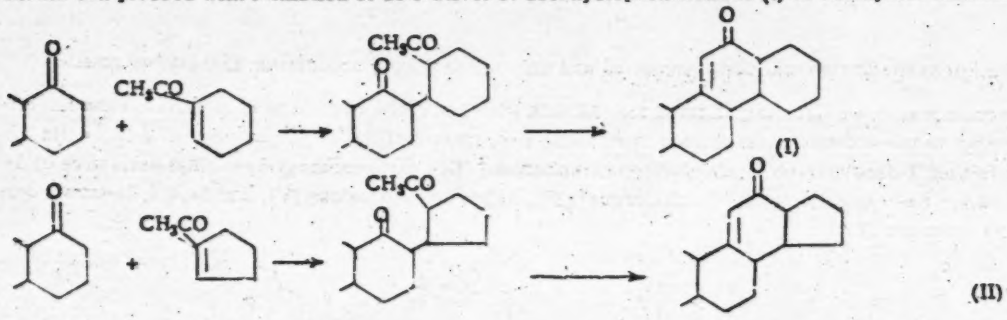
SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS

XIII. REACTION OF CARBOCYCLIC KETONES WITH 1-ACETYL-1-CYCLOHEXENE

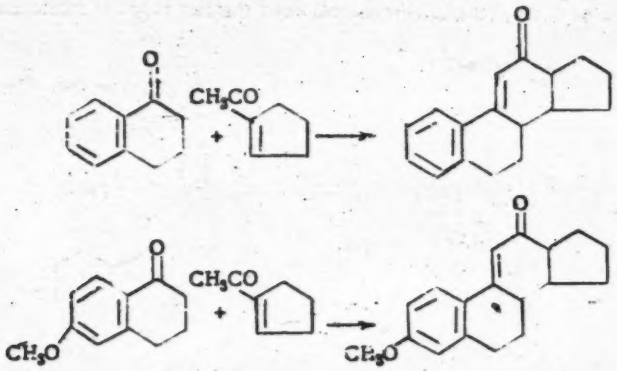
I.N.Nazarov and S.I.Zavyalov

It is known [1,2] that the reaction between cyclic ketones and 1-acetyl-cyclohexene or 1-acetyl-1-cyclopentene can proceed with formation of derivatives of decahydrophenanthrene (I) or octahydrobenzindan (II).

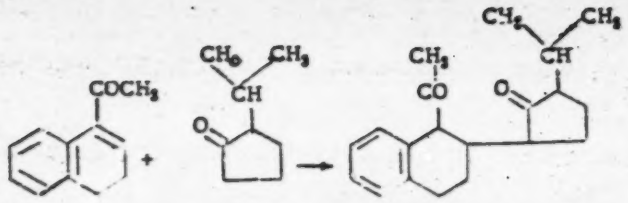


These reactions take place in two stages: first the saturated ketone under the influence of the alkaline catalyst adds at the double bond of the acetylcyclohexene or acetylcyclopentene according to a Michael type of reaction, and then the diketone formed cyclizes by means of an intramolecular crotonic condensation.

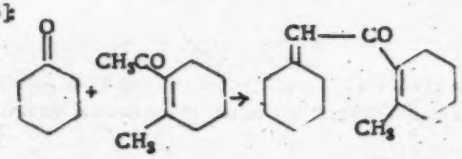
This method of building up polycyclic systems has been successfully applied to the synthesis of several polycyclic compounds related to steroids. Thus, from α-tetralone (3,4-dihydro-1(2H)-naphthalenone) and from 6-methoxy-α-tetralone it has been found possible to pass to compounds related in structure to estrone [1,2]:



In certain cases, when there is some obstacle in the way a Michael or crotonic condensation, the reaction between the cyclic ketone and 1-acetyl-1-cyclohexene stops at one of the stages and does not therefore lead to a polycyclic system. One such example is the reaction between 2-isopropyl-1-cyclopentanone and 1-acetyl-3,4-dihydronaphthalene [3]:

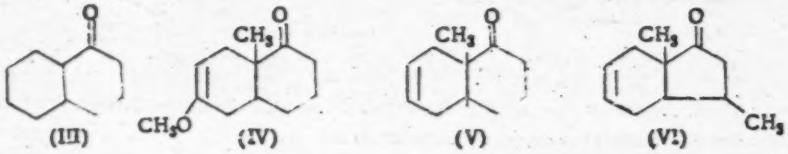


Here cyclization does not occur because of the blocking action of the isopropyl group on the keto group. It is true that under more severe conditions it has been possible to effect cyclodehydration by a special method also in this case. The reaction between cyclic ketones and derivatives of 1-acetyl-1-cyclohexene that are substituted in the 2-position is of particular interest [4,5]:



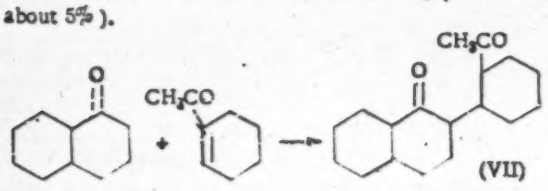
In this case the Michael addition reaction is inhibited and only the crotonic condensation is therefore possible.

In the present work we have investigated the reaction with 1-acetyl-1-cyclohexene of certain bicyclic ketones in an attempt to prepare substances related in structure to hormones of the androstane series. As bicyclic ketones we have used 1-decalone (octahydro-1(2H)-naphthalenone) (III), the 6-methoxy-8a-methyl derivative of 1-octalone (3,4,4a,5,8,8a-hexahydro-1(2H)-naphthalenone) (IV), 8a-methyl-1-octalone (V), and 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone (VI):



(III) (IV) (V) (VI)

These were converted by the aid of sodamide in ethereal solution into sodium derivatives, which were then submitted to the action of 1-acetyl-1-cyclohexene. In the case of 6-methoxy-8a-methyl-1-octalone (IV) we did not observe appreciable interaction, and the substances taken for reaction were recovered unchanged. In the remaining cases, high-boiling products were isolated in yields of 35-40%; in elementary composition they corresponded not to the tetracyclic ketones VII, X and XII, but to the compounds VII, IX, and XI, formed as a result of the Michael condensation; these have a ruptured C ring (the difference between the two types of substance in carbon content is about 5%).



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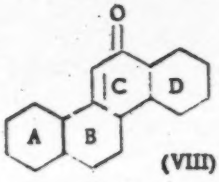

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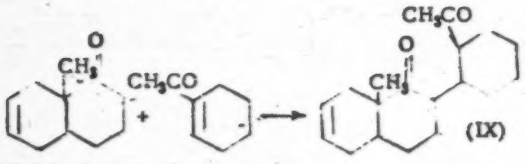

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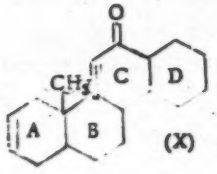

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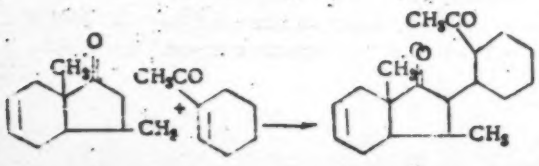

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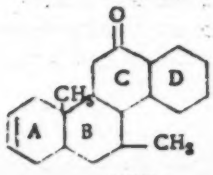

(XII)

The product of the reaction of 1-decalone with 1-acetyl-1-cyclohexene did not undergo hydrogenation in methanol solution in presence of a Pt catalyst, but treatment with excess of 2.4-dinitrophenylhydrazine gave the bis(2,4-dinitrophenylhydrazone). The reaction product from tetrahydro-3,7a-dimethyl-1-indanone and 1-acetyl-1-cyclohexene absorbed 1 molecular proportion of hydrogen at a Pt catalyst. Thus, under normal conditions intramolecular crotonic condensation of compounds VII, IX, and XI does not occur. The obstacle to this reaction is evidently the steric hindrance that is known to occur; it renders the keto group in ring B passive.

EXPERIMENTAL

1-Acetyl-1-cyclohexene (b.p. 85-87° at 15 mm; n_D^{20} 1.4900) was prepared by the condensation of acetyl chloride with cyclohexene in presence of stannic chloride and subsequent treatment of the reaction product with diethylaniline [6].

6-Methoxy-8a-methyl-1-octalone (IV) (b.p. 88-89° at 0.1 mm; n_D^{20} 1.5089) was prepared by the action of 2-methoxybutadiene on 2-methyl-2-cyclohexen-1-one [7].

cis-1-Decalone (III) (b.p. 113-114° at 15 mm; n_D^{20} 1.4900) was prepared by the oxidation of decahydro-1-naphthol [8].

Tetrahydro-3,7a-dimethyl-1-indanone (VI) (b.p. 90-92° at 7 mm; n_D^{20} 1.4875) was prepared by the condensation of butadiene with 2,4-dimethyl-2-cyclopenten-1-one [9].

8a-Methyl-1-octalone (V) (b.p. 70-73° at 3 mm; n_D^{20} 1.5042) was prepared by the action of butadiene on 2-methyl-2-cyclohexen-1-one [10].

The Reaction of 1-Decalone with 1-Acetyl-1-cyclohexene

A solution of 1-decalone (3 g; 1 mol) in dry ether (50 ml) and finely ground sodamide (0.8 g; 1 mol) were vigorously mixed together at room temperature for 7 hrs, a stream of dry hydrogen being passed through the reaction mixture. The solution was boiled on the water bath for 1 hr to remove residual ammonia. The suspension was cooled with ice, and 1-acetyl-cyclohexene (2.4 g; 1 mol) was added dropwise with stirring. Stirring with cooling was continued for a further 2 hrs. The mixture was then allowed to stand at room temperature overnight. Before further treatment, the reaction mixture was boiled on the water bath for 1½ hrs; the solution was then cooled with ice and treated with hydrochloric acid (diluted 1:1) until weakly acid to Congo red. The ether layer was separated and dried with sodium sulfate. The ether was driven off, and the residue was vacuum-distilled. The reaction product VII (1.9 g) was obtained; b.p. 172-178° at 2 mm.

Found %: C 78.07; 78.49; H 10.26; 10.10
$C_{18}H_{28}O_2$. Calculated %: C 78.26; H 10.15

The substance did not hydrogenate in methanol solution in presence of a Pt catalyst, but it reacted with excess of 2,4-dinitrophenylhydrazine to give the bis(2,4-dinitrophenylhydrazone), which melted with decomposition at 213-215° (from benzene).

Found %: N 17.79; 17.83
$C_{32}H_{36}O_8N_8$. Calculated %: N 17.61

The Reaction of 8a-Methyl-1-octalone with 1-Acetyl-1-cyclohexene

8a-Methyl-1-octalone (V) (2 g; 1 mol) in dry ether (40 ml), finely ground sodamide (0.5 g; 1 mol), and 1-acetyl-1-cyclohexene (1.5 g; 1 mol) were taken for reaction. The reaction product (1.2 g) was IX, b.p. 153-157° at 0.05 mm; n_D^{20} 1.5412.

Found %: C 78.87; 78.84; H 10.08; 10.02
$C_{19}H_{28}O_2$. Calculated %: C 79.16; H 9.73

The 2,4-dinitrophenylhydrazone melts at 215-217° with decomposition (from benzene):

Found %: N 11.84; 11.77
$C_{25}H_{32}O_5N_4$. Calculated %: N 11.9

Reaction of 3a, 4, 7, 7a-tetrahydro-3, 7a-dimethyl-1-indanone with 1-Acetyl-1-cyclohexene

3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone (VI) (3 g; 1 mol.) in dry ether (50 ml), finely ground sodamide

(0.72 g; 1 mol), and 1-acetyl-1-cyclohexene (2.2 g; 1 mol) were taken for reaction. The experiment was carried out as described above. The reaction product (2.2 g) was XI, b.p. 166-170° at 2 mm; n_D^{20} 1.5395.

Found %: C 78.80; 78.89; H 9.51; 9.43
$C_{19}H_{28}O_2$. Calculated %: C 79.16 H 9.73

The 2,4-dinitrophenylhydrazone melts at 223-224° with decomposition (from benzene):

Found %: N 12.2; 11.98
$C_{25}H_{32}O_5N_4$. Calculated %: N 11.9

On hydrogenation in methanol solution at a Pt catalyst the substance absorbs 1 mol of hydrogen.

Attempt to Condense 6-Methoxy-8a-methyl-1-octalone with 1-Acetyl-1-cyclohexene

A solution of the sodium derivative of 6-methoxy-8a-methyl-1-octalone, prepared from the ketone (IV) (3 g; 1 mol), finely ground sodamide (0.6 g; 1 mol), and dry ether (50 ml), was treated with 1-acetyl-1-cyclohexene (1.9 g; 1 mol) under the conditions described above. The original substances and some resinous products (0.4 g) were isolated from the reaction mixture.

SUMMARY

The condensation has been carried out of 1-decalone (III), 8a-methyl-1-octalone (V), and 3a,4,7,7a-tetrahydro-3,7a-dimethyl-1-indanone (VI) with 1-acetyl-1-cyclohexene. The products were the polycyclic diketones VII, IX, and XI, which under the conditions of the experiment did not undergo a further intramolecular crotonic condensation.

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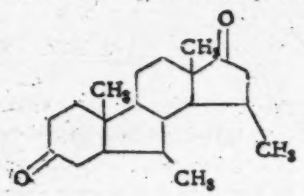
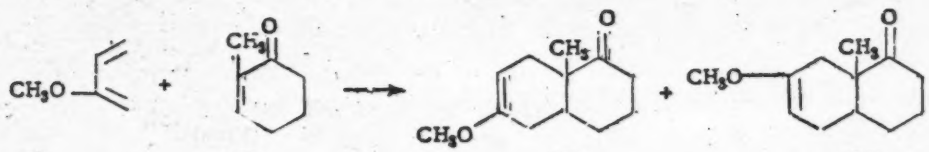
COMMUNICATION 126. SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO STEROIDS. XIV. SYNTHESIS OF TETRACYCLIC KETONES HAVING A METHYLCYCLOPENTANE B RING

L. N. Nazarov, V. F. Kucherov, and L. N. Terekhova

As already shown [1], it is possible to proceed from 2,4-dimethyl-2-cyclopenten-1-one (V) by means of diene condensations and via the intermediate compounds VI, VIII, and X to the synthesis of a tetracycloketone, which has a β-norandrostane skeleton and was provisionally assigned the structure of a normal steroid ketone:



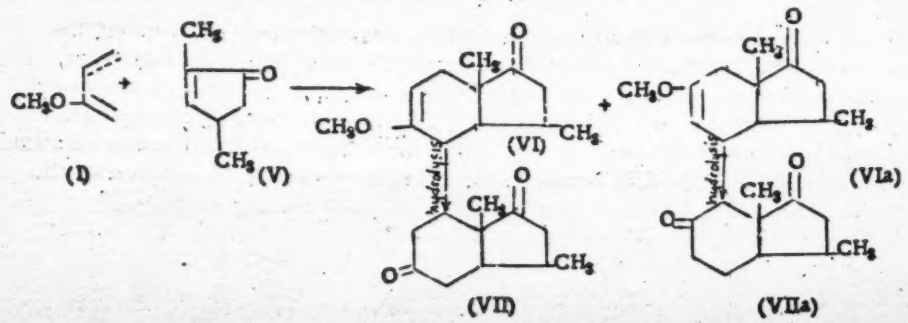
However, subsequent detailed study of the diene synthesis has shown that condensation of 2-methoxybutadiene with unsaturated cyclic ketones such as 2-methyl-2-cyclohexen-1-one leads to a mixture of para and meta condensation products, with predominant formation of the normal addition product, which has the methoxy group in the para-position to the angular methyl group. In this work the example was taken of the condensation of 2-methoxybutadiene (I) with 2-methyl-2-cyclohexen-1-one (II), and it was shown that the main liquid product of the diene condensation, which has a narrow boiling range and a constant refractive index, contains, in addition to the main product of normal condensation cis-6-methoxy-8a-methyl-1-octalone (cis-3,4,4a,5,8,8a-hexahydro-6-methoxy-8a-methyl-1(2H)-naphthalenone) (III), about 5% of the meta isomer (IV):



(I) (II) (III) (IV)

The meta isomer (IV) that was formed could not be isolated by fractional distillation, and its presence and structure were demonstrated after its conversion into the corresponding crystalline acetylenic hydroxy ketones. The condensation of 2-methoxybutadiene (I) with 2,4-dimethyl-2-cyclopenten-1-one (V) proceeds in similar fashion, and this forms the subject of the present communication.

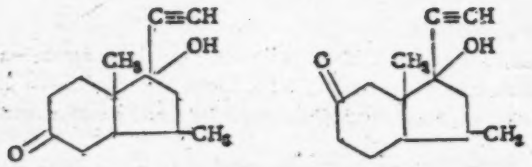
2-Methoxybutadiene (I) heated with a 25-30-fold excess of 2-4-dimethyl-2-cyclopenten-1-one (V) at 230° for 1.5 hr and then carefully distilled under reduced pressure yields cis-3a,4,7,7a-tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI), b.p. 103-104° at 1.5 mm and n_D^{20} 1.4960, in 25-30% yield. However, the product obtained is not an individual compound, and after hydrolysis into the corresponding diketone (VII) a mixture of disemicarbazones can be made and separated by crystallization:



(I) (V) (VI) (VIa) (VII) (VIIa)

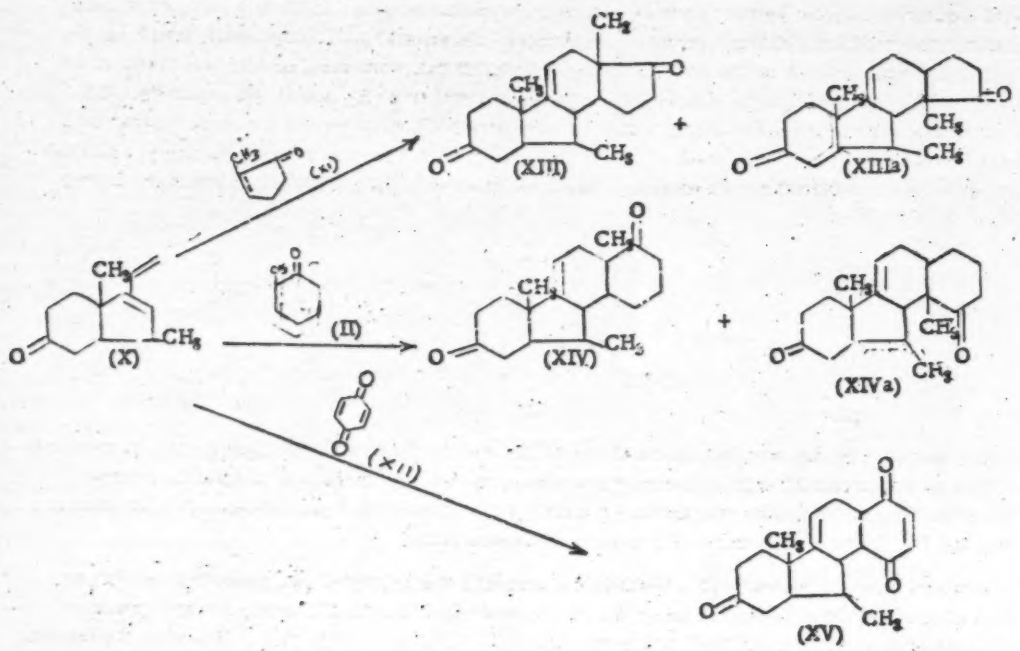
Condensation of the methoxytetrahydroindanone (VI) (b.p. 103-104° 1.5 mm; n_D^{18} 1.4960) with acetylene in liquid ammonia in presence of metallic potassium and subsequent acid hydrolysis of the product gave a 25% yield of a crystalline acetylenic compound (VIII), m.p. 135-136°, which has been described previously [1]. From the liquid portion formed in the acetylene synthesis it was found possible by fractional distillation and treatment with ether and with petroleum ether (see Experimental part) to isolate another similar product (IX), m.p. 118-119.5° and giving a semicarbazone m.p. 200-201°, in 6% yield.

According to the results obtained in our laboratory on the condensation of 2-methoxybutadiene and 2-methyl-2-cyclohexen-1-one, the main acetylenic product, m.p. 135-136°, will be 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-1-5(4H)-indanone (VIII), and the other isomer, which is formed in small amount, will be 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-6(5H)-indanone (IX):



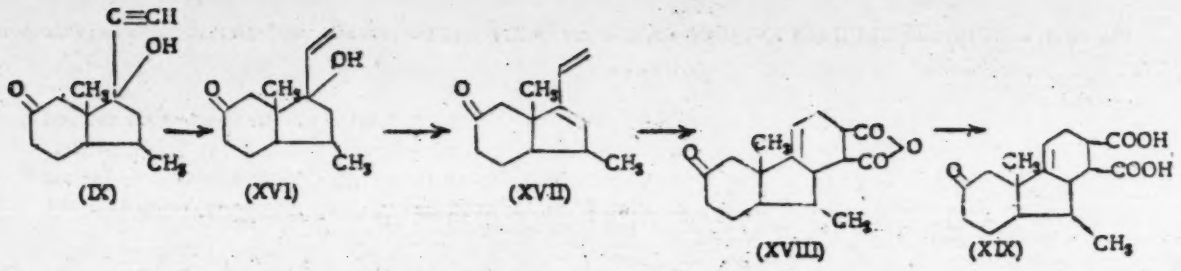
(VIII) (IX)

The main product (VIII) is converted by selective hydrogenation over a Pd catalyst and subsequent dehydration into the previously described 3a, 4,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (X), which on condensation with 2-methyl-2-cyclopenten-1-one (XI) or with 2-methyl-2-cyclohexen-1-one (II) yields in 60% yield the tetracyclic ketone XIII or XIV respectively, in the form of a viscous glasslike product which is a mixture of two possible structural forms (XIII and XIIIa; XIV and XIVa).



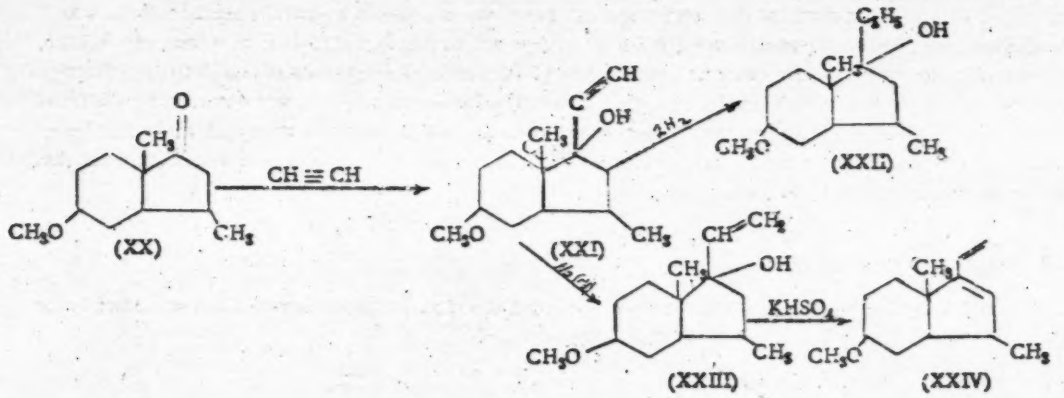
Condensation of the vinyltetrahydroindenone (X) with p-quinone (XII) gives a high yield of the individual substance (XV), which on hydrogenation over a Pt catalyst absorbs about 2 moles of hydrogen.

The isomeric acetylenic hydroxy ketone (IX) gives, on selective hydrogenation over a Pd catalyst, the corresponding tetrahydro-1-hydroxy-3,7a-dimethyl-1-vinyl-6(5H)-indanone (XVI) (m.p. 88-89°; semicarbazone, m.p. 166-167.5°), which on dehydration over potassium hydrogen sulfate yields 3,3,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-6(4H)-indenone (XVII), characterized as its crystalline semicarbazone, m.p. 187-188°. On condensation with maleic anhydride, the vinyltetrahydroindenone (XVII) gives the tricyclic fluorenedicarboxylic anhydride (XVIII), from which on hydrolysis is obtained the corresponding decahydro-4b, 9-dimethyl-6-oxofluorene-1,2-dicarboxylic acid (XIX):

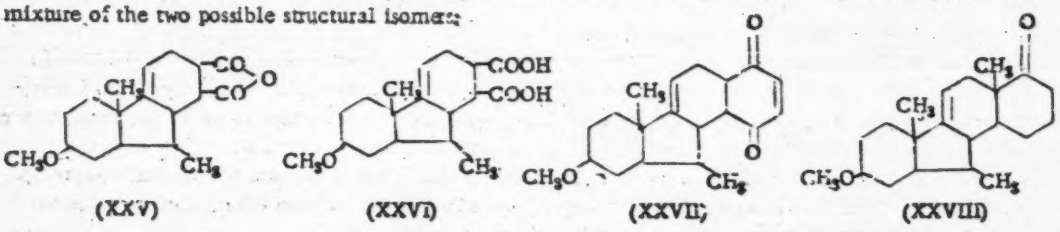


When the main methoxytetrahydroindanone (VI) is hydrogenated in alcohol at room temperature over a Pd catalyst, about 80% of the required amount of hydrogen is absorbed, and a non-homogeneous reaction product is obtained: 80-108° at 2 mm; n_D^{20} 1.4780-1.4820*. After careful fractionation, the main hydrogenation product, b.p. 94-98° at 2 mm; n_D^{20} 1.4785, may be isolated in about 60% yield; this has been described previously [1], and it corresponds in composition to hexahydro-5-methoxy-2,7a-dimethyl-1-indanone (XX), but is not an individual substance. When it is condensed with acetylene in liquid ammonia in presence of metallic potassium, a crystalline acetylenic methoxy alcohol, m.p. 114-115°, is obtained in about 35% yield; in accordance with our previous results, this compound has the structure 1-ethynylhexahydro-5-methoxy-3,7a-dimethyl-1-indanol (XXI). The other isomeric acetylenic alcohol could not be isolated.

When the acetylenic methoxy alcohol (XXI) was exhaustively hydrogenated, 2 moles of hydrogen were absorbed, and the ethylmethoxy alcohol (XXII) was obtained. Selective hydrogenation of the acetylenic methoxyhexahydroindanol (XXI) over a Pd catalyst yielded a liquid vinyl compound (XXIII), which gave by dehydration over potassium hydrogen sulfate 3a,4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) in good yield.



On condensation with maleic anhydride, the diene (XXIV) gives with 40% yield the tricyclic methoxyfluorenedicarboxylic anhydride (XXV), which yields on hydrolysis the corresponding 1,2,3,4b,5,6,7,8,8a,9a-decahydro-7-methoxy-4b,9-dimethylfluorene-1,2-dicarboxylic acid (XXVI). The diene (XXIV) condenses with p-quinone to give the crystalline tetracyclic product (XXVII), which does not undergo hydrogenation over a Pd catalyst under normal conditions. When the diene (XXIV) is condensed with 2-methyl-2-cyclohexen-1-one (II), the corresponding tetracyclic product (XXVIII) is formed as a viscous glasslike mass, which appears to be a mixture of the two possible structural isomers:



* When more severe hydrogenation conditions are used (with heating and under a hydrogen pressure of 100 atm), partial hydrogenation of the carbonyl group occurs.

The tetracyclic ketones (XXVII) and (XXVIII) do not give crystalline semicarbazones and 2,4-dinitrophenylhydrazones.

EXPERIMENTAL

2,4-Dimethyl-2-cyclopenten-1-one (V) (b.p. 53-55° at 10 mm; n_D^{20} 1.4655) was prepared by the method developed in our laboratory, i.e. by the cyclization of allyl isopropenyl ketone [2]. 2-Methoxy-1,3-butadiene [1] (b.p. 75-76°; n_D^{20} 1.4435) was obtained by the splitting of methanol from 1,3,3-trimethoxybutane by the aid of sodium hydrogen sulfate [3]. The conditions of this synthesis, as improved in our laboratory, result in a 75% yield of 2-methoxybutadiene.

I. Condensation of 2-Methoxy-1,3-butadiene with 2,4-Dimethyl-2-cyclopenten-1-one

A mixture of 2,4-dimethyl-2-cyclopenten-1-one (550 g), 2-methoxybutadiene (20 g), and pyrogallol (2 g) was heated in a steel autoclave at 230° for 1½ hr. The mixture was cooled rapidly, more 2-methoxybutadiene (20 g) was added, and the mixture was again heated at 230° for 1½ hr. The reaction product after vacuum fractionation yielded 410 g of the original 2,4-dimethyl-2-cyclopenten-1-one (n_D^{20} 1.4650), 95 g of the isomeric 2,4-dimethyl-4-cyclopenten-1-one (n_D^{20} 1.4735) and 38 g of a condensation product having b.p. 95-140° at 2 mm (n_D^{20} 1.4965).

From 208 g of condensation product obtained in different experiments there was isolated, after fractionating twice through a column, 100 g of 3a, 4,7,7a-tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI) [1], b.p. 103-104° at 1.5 mm; n_D^{20} 1.4960. It could not be purified further by repeated distillation.

II. Hydrolysis of 3a,4,7,7a-Tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone

The methoxytetrahydroindanone (VI) (20 g) was stirred vigorously at room temperature with 3% hydrochloric acid (60 ml) for 5 hrs. The mixture was neutralized with potassium carbonate, saturated with ammonium chloride, and carefully extracted with ether. The ether extract was dried with sodium sulfate, the ether driven off, and the residue vacuum-distilled through a column. From the mixture of hydrolysis products there was separated, after three successive distillations, 6.5 g of a substance having b.p. 119-121° at 2 mm; n_D^{20} 1.4925, and corresponding to the previously described tetrahydro-3,7a-dimethyl-1,5(4H)-indandione (VII) [1]. From this diketone (1.1 g) the disemicarbazone (1 g), m.p. 210-217° with decomposition, was obtained by the usual method. After being boiled with 20 times its amount of methanol, the undissolved substance melted at 240-245° (dec.). By recrystallization from a large volume of methanol, this disemicarbazone was obtained in the form of fine needles, m.p. 253-254° (dec.).

Found %: N 28.13
$C_{13}H_{22}O_2N_6$. Calculated %: N 28.40

A second disemicarbazone was isolated by evaporating down the methanol mother liquor. After being recrystallized from methanol it melted at 224-225° (dec).

Found %: N 28.10
$C_{13}H_{22}O_2N_6$. Calculated %: N 28.40

A mixed test of these two disemicarbazones gave a m.p. of 234-236° (dec).

III. Condensation of 3a,4,7,7a-Tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI) with Acetylene

Liquid ammonia (950 ml) was poured into a three-necked flask, provided with a stirrer, dropping funnel, reflux condenser, and tube for the passage of acetylene, and cooled to −70° by means of a mixture of solid carbon dioxide and acetone. Metallic potassium (50 g) was added slowly. Dry acetylene (300 liter) was then passed over a period of 2 hrs, and at −70° a solution of 3a,4,7,7a-tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI, 100 g) in absolute ether (200 ml) was added over 1.5 hr. The mixture was stirred by passage of a feeble stream of acetylene for 4 hrs, and was left overnight at −70°. On the next day it was stirred for a further 10 hrs at this temperature, and on the following day the ammonia was evaporated off. The residue was decomposed at −10° by addition of dry ammonium chloride (100 g); a further addition of ether (200 ml) was made, and water was added until the precipitate dissolved. The ether layer was separated, and the water layer extracted twice with ether. The united ether extracts were washed with a small amount of water, and the ether was driven off.

A 2% solution of hydrochloric acid (100 ml) was added to the residue, and the mixture was stirred

vigorously at room temperature for 5 hrs. The crystalline product that was precipitated was filtered off and washed with 30% methanol. A substance (21.5 g) m.p. 134-136°, identical with the previously described acetylenic hydroxy ketone (VIII) [1] was obtained. The liquid product was extracted with ether, and the ether extract was washed with bicarbonate solution and dried. The residue remaining after driving off the ether was vacuum-distilled at 0.02 mm. The following fractions were obtained:

Fraction 1, b.p. 75-100°; n_D^{20} 1.4960; 15 g;

Fraction 2, b.p.100-110°; n_D^{20} 1.4995; 5 g ;

Fraction 3, b.p.110-125°; n_D^{20} 1.5070; 52.5 g.

After addition of a small amount of absolute ether, fraction 3 gradually began to crystallize. After 5 days, the crystals that had separated were filtered off and washed with absolute ether. A further 4.8 g of the acetylenic hydroxy ketone, m.p. 134-136°, was obtained. The total yield of the acetylenic hydroxy ketone (VIII)(1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-5(4H)-indanone)was 26.3 g (25% of theoretical).

From the ethereal solution, after addition of a small amount of petroleum ether and cooling, fine needle-like crystals separated and were filtered off after 5 days. 3 g of a substance melting at 110-114° was obtained. After removal of the solvents by distillation and vacuum fractionation of the residue, a fraction (29 g) was isolated having b.p. 145-150° at 2 mm; n_D^{20} 1.5090, from which by treatment with a mixture of petroleum ether and ethyl ether (1:1), with cooling and prolonged standing (10-15 days), a further 3.2 g of substance, m.p. 108-112°, was isolated.

The total yield of the second crystalline product was 6.2 g (5.8%), and after crystallization from acetone it had the constant m.p. 118-119.5°. Analysis showed the product to have a composition corresponding to 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-5(4H)-indanone (IX).

Found %: C 75.90; 75.90; H 8.83; 8.67

$C_{13}H_{18}O_2$. Calculated %: C 75.70; H 8.80

It was not found possible to isolate other individual products of the acetylene synthesis.

IV. Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (X) with 2-Methyl-2-cyclopenten-1-one (XI)

A mixture of the diene (X) (1.4 g) (98-100° at 3 mm; n_D^{20} 1.5048), which has been described previously [1] and was prepared from the acetylenic alcohol (VIII,) 2-methyl-2-cyclopenten-1-one (XI, 16.4 g) (b.p. 52-53° at 15 mm; n_D^{20} 1.4770) and pyrogallol (0.1 g) was heated at 170° in a glass ampoule for 5 hrs. Vacuum distillation yielded 2-methyl-2-cyclopenten-1-one (14.7 g), the original diene (X) (0.9 g) and the tetracyclic diketone (XIII) (1 g) as a thick pale-yellow liquid, b.p. 170-180° at 0.02 mm; n_D^{20} 1.5370.

Found %: C 79.75; 79.92; H 9.14; 9.13

$C_{19}H_{26}O_2$. Calculated %: C 79.70; H 9.10

The disemicarbazone of the tetracyclic diketone (XIII) melted after recrystallization from alcohol at 201-202° (dec).

Found %: N 20.90; 21.17

$C_{21}H_{32}O_2N_6$. Calculated %: N 21.0

When the tetracyclic diketone (XIII) was hydrogenated in alcohol over a Pt catalyst, 1 molecular equivalent of hydrogen was absorbed, and the hydrogenation product was separated as a colorless glass-like substance, b.p. 130-140° at 0.012 mm; n_D^{20} 1.5320.

Found %: C 79.16; 78.97; H 10.08; 10.10

$C_{19}H_{28}O_2$. Calculated %: C 79.16; H 9.73

V. Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (X) with 2-Methyl-2-cyclohexen-1-one (II)

A mixture of the diene (X) (1.6 g), 2-methyl-2-cyclohexen-1-one (II, 22.5 g) (b.p. 65-67° at 16 mm; n_D^{22} 1.4810), and pyrogallol (0.1 g) was heated at 170° in a glass ampoule for 5 hrs. Vacuum distillation yielded 2-methyl-2-cyclohexen-1-one (21 g), the original diene (X) (1.1 g), and the tetracyclic diketone (XIV) (0.68 g) as a viscous liquid, b.p. 143-150° at 0.013 mm; n_D^{20} 1.5375.

Found %: C 79.95; 80.20; H 9.20; 9.24;
$C_{20}H_{28}O_2$. Calculated %: C 80.00 H 9.30

When the tetracyclic diketone(XIV)was hydrogenated in alcohol over a Pt catalyst, 2 molecular equivalents of hydrogen was absorbed, and the hydrogenation product was obtained as a colorless viscous liquid, b.p. 150-160° at 0.02 mm; n_D^{20} 1.5330.

Found %: C 78.70; 78.66; H 10.24; 10.20
$C_{20}H_{32}O_2$. Calculated %: C 78.95; H 10.53

VI. Condensation of 3a,4,7,7a-Tetrahydro-1,3a-dimethyl-3-vinyl-6(5H)-indenone (X) with p-Quinone (XII)

The diene (X) (2 g), p-quinone (1.05 g), and pyrogallol (0.05 g) were dissolved in absolute dioxane (15 ml) and heated at 60° for 5 hrs. The dioxane was driven off, and a crystalline product (1.8 g) of m.p. 134-139° was obtained. Crystallization from methanol yielded the pure tetracyclic triketone(XV) m.p. 136-137°.

Found %: C 76.88; 76.61; H 7.51; 7.48
$C_{12}H_{22}O_3$. Calculated %: C 76.51; H 7.38

With semicarbazide the tetracyclic triketone(XV)gave a disemicarbazone that did not melt below 300°. It was purified by reprecipitation by water from methanol solution.

Found %: N 19.90; 20.09
$C_{21}H_{28}O_3N_6$. Calculated %: N 20.38

VII. Selective Hydrogenation of 1-Ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-6(5H)-indanone (IX)

The acetylenic hydroxytetrahydroindanone(IX)(2.55 g), m.p. 117-118°, was dissolved in absolute dioxane (10 ml) and hydrogenated over a Pd catalyst at 22° and 742 mm. When 310 ml of hydrogen had been absorbed (305 ml would be required for one double bond), the catalyst was filtered off, and the dioxane driven off under reduced pressure. The crystalline product was mixed with petroleum ether and then filtered off. 2.25 g of a substance melting at 84-86° was obtained. After crystallization from petroleum ether, tetrahydro-1-hydroxy-3,7a-dimethyl-1-vinyl-6(5H)-indanone (XVI) had m.p. 88-89°.

Found %: C 75.50; 75.30; H 9.71; 9.67
$C_{12}H_{20}O_2$. Calculated %: C 75.20; H 9.62

The semicarbazone was obtained after crystallization from 40% methanol as fine needles, m.p. 166-167.5°.

Found %: N 15.51; 15.77
$C_{13}H_{23}O_2N_3$. Calculated %: N 15.83

VIII. Dehydration of Tetrahydro-1-hydroxy-3,7a-dimethyl-1-vinyl-6(5H)-indanone (XVI)

A mixture of the vinylhydroxy ketone(XVI)(1.7 g) and finely ground anhydrous potassium hydrogen sulfate (0.8 g) was heated in a Claisen flask at 120° under a pressure of 80 mm for 20 min. The dehydration product was extracted with ether, the ethereal solution dried over anhydrous magnesium sulfate, and the ether driven off. By distillation under reduced pressure, the residue yielded 3a,6,7,7a-tetrahydro-1,3a-dimethyl-3-vinyl-5(4H)-indenone (XVII), b.p. 125-130° at 7 mm; n_D^{20} 1.5160. The diene(XVII)rapidly turned yellow on standing, becoming a thick yellow mass. It was characterized as its crystalline semicarbazone, which after crystallization from 80% methanol melted at 187-188°.

Found %: N 17.40
$C_{14}H_{21}ON_3$. Calculated %: N 17.08

IX. Condensation of 3a,6,7,7a-Tetrahydro-1,3a-dimethyl-3-vinyl-5(4H)-indenone (XVII) with Maleic Anhydride

A mixture of the diene XVII (0.55 g) and maleic anhydride (0.3 g) was heated in a glass ampoule at 120-125° for 3 hrs. After cooling and standing for a long time (20 days), the reaction product partially

crystallized out. After treatment with a mixture of benzene and petroleum ether (1:1), the crystalline product was filtered off. The tricyclic fluorenedicarboxylic anhydride XVIII (0.25 g) was obtained; m.p. after crystallization from a mixture of benzene and petroleum ether: 206-207°.

Found %: C 70.89; 70.99; H 7.05; 7.02
$C_{17}H_{16}O_4$. Calculated %: C 70.83; H 6.94

The anhydride XVIII (0.1 g) was hydrolyzed by boiling it with 2% HCl (4 ml) until it was almost completely dissolved (3 hrs). The hot filtered solution gave, on cooling, a fine crystalline precipitate of m.p. 226-230°. After crystallization from 40% ethanol, 1,2,3,4b,5,6,7,8,8a,9a-decahydro-4b,9-dimethyl-6-oxofluorene-1,2-dicarboxylic acid (XIX) had m.p. 236-238° (dec).

Found %: C 65.91; 66.04; H 7.26; 7.45
$C_{17}H_{22}O_5$. Calculated %: C 66.45; H 7.20

X. Hydrogenation of 3a,3,7,7a-Tetrahydro-5-methoxy-3,7a-dimethyl-1-indanone (VI)

The methoxytetrahydroindanone VI (n_D^{20} 1.4960) (10 g) was dissolved in absolute dioxane (20 ml) and hydrogenated over a Pd catalyst at 20° and 738 mm. The amount of hydrogen absorbed (930 ml in 17 hrs) corresponded to 80% of the theoretical quantity. On addition of fresh catalyst, no further hydrogenation occurred. The catalyst was filtered off, the solvent driven off, and the liquid hydrogenation product vacuum-distilled. By a double distillation through a column, a substance (6.7 g, b.p. 84-98° at 2 mm, n_D^{20} 1.4785) was isolated which was found to be the previously described [1] hexahydro-5-methoxy-3,7a-dimethyl-1-indanone (XX).

XI. Condensation of Hexahydro-5-methoxy-3,7a-dimethyl-1-indanone with Acetylene

Liquid ammonia (250 ml) was poured into a three-necked flask cooled to −70° and provided with a stirrer, thermometer, dropping funnel, and tube for the passage of acetylene. Metallic potassium (14 g) was added slowly with stirring, and acetylene was then passed for 30 min (150 liter). A solution of hexahydro-5-methoxy-3,7a-dimethyl-1-indanone (XX) (25 g) in absolute ether (20 ml) was added slowly (over 1 hr). The mixture was stirred at −70° with passage of a feeble stream of acetylene for 5 hrs, and was then left overnight. On the next day stirring was continued for a further 10 hrs, and the mixture was again left overnight. The ammonia was evaporated off, and the reaction product was decomposed at not above 0° by addition of ammonium chloride (35 g); ether (100 ml) was added, and then water until the precipitate present was dissolved. The ether layer was separated, and the aqueous part was extracted twice with ether; the united ether extracts were washed with a small amount of cold water, and then dried over magnesium sulfate. After removal of the ether the residue crystallized out (on standing), giving a half-solid mass. The crystalline product was filtered off and washed with a small amount of cold ether. The acetylenic alcohol XXI (7.2 g, m.p. 111-113°) was obtained. The liquid reaction product was freed from solvent and vacuum-distilled. The following fractions were obtained:

Fraction 1, b.p. 75-110° at 1.5 mm; n_D^{22} 1.4820; 3 g

Fraction 2, b.p. 110-135° at 1.5 mm; n_D^{22} 1.4980; 10 g

By treatment of fraction 2 with petroleum ether and cooling of the solution obtained, a further 2.1 g of crystals m.p. 111-113° was obtained. The total yield of the crystalline product of the acetylene synthesis was 9.3 g, i.e. 33.5% of theoretical. After crystallization from petroleum ether the 1-ethynylhexahydro-5-methoxy-3,7a-dimethyl-1-indanol (XXI) obtained had m.p. 114-115°.

Found %: C 75.81; 75.76; H 10.22; 10.33
$C_{14}H_{22}O_2$. Calculated %: C 75.65; H 10.00

It was not found possible to separate other individual substances from the liquid product of the acetylene synthesis.

XII. Hydrogenation of 1-Ethynyl-hexahydro-5-methoxy-3,7a-dimethyl-1-indanol (XXI)

a) The acetylenic methoxyhexahydroindanol XXI (1.5 g) was exhaustively hydrogenated in dioxane solution over a Pd catalyst and yielded by distillation the ethylmethoxy alcohol XXII (1.2 g) having b.p. 116-117° at 2.5 mm; n_D^{20} 1.4870; d_4^{20} 0.9920; found MR_D 65.64; calculated MR_D for $C_{14}H_{24}O_2$ 65.62.

Found %: C 74.26; 74.05; H 11.75; 11.62
$C_{14}H_{26}O_2$. Calculated %: C 74.28; H 11.58

b) The acetylenic methoxyhexahydroindanol(XXII)(3.6 g) was dissolved in absolute dioxane (30 ml) and hydrogenated over a Pd catalyst at 22° and 7[illegible] mm. The hydrogenation was stopped when 415 ml of hydrogen had been absorbed (400 ml of H_2 is required for one double bond), the catalyst was filtered off, the dioxane was driven off, and the residue was vacuum-distilled. The product was hexahydro-5-methoxy-3,7a-dimethyl-1-vinyl-1-indanol (XXIII) (3.2 g) having b.p. 120-121° at 2.5 mm; n_D^{20} 1.4970; d_4^{20} 1.0118; found MR_D 64.88; calculated MR_D 65.15.

Found %: C 74.40; 74.60; H 11.10; 11.10
$C_{14}H_{24}O_2$. Calculated %: C 74.95; H 10.74

XIII. Dehydration of Hexahydro-5-methoxy-3,7a-dimethyl-1-vinyl-1-indanol (XXIII)

A mixture of the vinylmethoxyhexahydroindanol(XXIII)(4.6 g) and finely ground anhydrous potassium hydrogen sulfate (2.3 g) was heated in a Claisen flask at 120-130° under a pressure of 80 mm for 30 min. The water was driven off, and the dehydration product was vacuum-distilled yielding 3a,4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) (3.3 g), b.p. 110-111° at 7 mm; n_D^{20} 1.4980. The diene obtained (XXIV) is extremely unstable, and it was used directly for further diene condensations.

XIV. Condensation of 3a,4,5,6,7,7a-Hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) with Maleic Anhydride

A mixture of the diene(XXIV)(0.9 g) and maleic anhydride (0.45 g) was heated in a glass ampoule at 120° for 2.5 hrs. After standing for 2 days, the reaction product partially crystallized out; the crystals were filtered off and washed with petroleum ether. After crystallization from petroleum ether containing a little benzene, the tricyclic fluorenecarboxylic anhydride(XXV)(0.4 g) was obtained as colorless needles m.p. 115-116°.

Found %: C 70.76; 70.96; H 8.21; 8.18
$C_{18}H_{24}O_4$. Calculated %: C 71.00; H 7.95

The anhydride(XXV)(0.25 g) was hydrolyzed by boiling for 3 hrs with 3% HCl (3 ml). After the solution had cooled, the crystalline product was filtered off and washed with water. After crystallization from 50% alcohol, 0.2 g was obtained of 1,2,3,4b,5,6,7,8,8a,9a-decahydro-7-methoxy-4b,9-dimethylfluorene-1,2-dicarboxylic acid (XXVI), m.p. 216-217°.

Found %: C 67.17; 67.22; H 8.46; 8.70
$C_{18}H_{26}O_5$. Calculated %: C 67.05; H 8.44

XV. Condensation of 3a,4,5,6,7,7a-Hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) with p-Quinone (XII)

The diene(XXIV)(0.8 g) and p-quinone (0.4 g) were dissolved in absolute dioxane (10 ml) and heated at 60-65° for 5 hrs. The viscous yellow reaction product that remained after removal of solvent was vacuum-distilled, and a substance (0.5 g) of b.p. 135-150° at 0.02 mm was obtained. Treatment with a small amount of cold alcohol gave the crystalline tetracyclic diketone(XXVII,)which after crystallization from 80% alcohol had m.p. 125-126°.

Found %: C 75.62; 75.70; H 8.15; 8.40
$C_{20}H_{26}O_3$. Calculated %: C 76.30; H 8.35

The tetracyclic diketone(XXVII)does not give crystalline derivatives with semicarbazide or with 2,4-dinitrophenylhydrazine and is not hydrogenated in presence of a Pd catalyst.

XVI. Condensation of 3a,4,5,6,7,7a-Hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV) with 2-Methyl-2-cyclohexen-1-one (II)

The diene(XXIV)(1.1 g) was dissolved in 2-methyl-2-cyclohexen-1-one (15 g) and heated in a glass ampoule at 180° for 5 hrs. The products of distillation were 2-methyl-2-cyclohexen-1-one (13.2 g), the original diene (0.4 g) and the tetracyclic ketone(XXVIII)(0.52 g) as a light-yellow, glasslike liquid, b.p. 135-150° at 0.015 mm.

Found %: C 79.24; 79.27; H 10.50; 10.65
$C_{22}H_{32}O_2$. Calculated %: C 79.60; H 10.25

The tetracyclic ketone(XXVIII)does not give a crystalline semicarbazone or 2,4-dinitrophenylhydrazone.

SUMMARY

1. Heating of 2-methoxy-1,3-butadiene (I) with 2,4-dimethyl-2-cyclopenten-1-one (V) yields as the main product the methoxytetrahydroindanone (VI), but there is formed in small amount also the isomeric methoxytetrahydroindanone (VIa). On condensation of the mixture (VI + VIa) with acetylene in liquid ammonia and subsequent hydrolysis of the product, there are obtained two crystalline acetylenic hydroxy ketones, 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-5(4H)-indanone (VIII, and 1-ethynyltetrahydro-1-hydroxy-3,7a-dimethyl-6(5H)-indanone (IX). A number of derivatives were prepared from the latter – the vinylhydroxy ketone(XVI) the dienone(XVII) the anhydride(XVIII), and the keto acid(XIX).

2. By condensation of the previously described dienone X with 2-methyl-2-cyclopenten-1-one (XI), with 2-methyl-2-cyclohexen-1-one (II), and with p-quinone (XII), the steroid tetracyclic ketones(XIII, XIV, and XV) having a five-membered B ring have been prepared.

3. By condensation of hexahydro-5-methoxy-3,7a-dimethyl-1-indanone (XX) with acetylene in liquid ammonia, 1-ethynylhexahydro-5-methoxy-3,7a-dimethyl-1-indanol (XXI) was prepared, and from this there were obtained the compounds hexahydro-5-methoxy-3,7a-dimethyl-1-vinyl-1-indanol (XXIII) and 3a,4,5,6,7,7a-hexahydro-6-methoxy-1,3a-dimethyl-3-vinylindene (XXIV).

4. By condensation of the diene (XXIV) with maleic anhydride, with p-quinone, and with 2-methyl-2-cyclohexen-1-one there were obtained the tricyclic anhydride (XXV), the acid (XXVI), and the tetracyclic methoxy ketones(XXVII and XXVIII).

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Institute of Organic Chemistry of the
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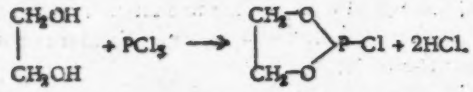
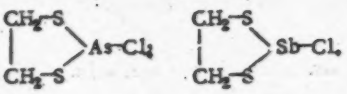
ETHYLENE ESTER OF PHOSPHOROCHLORIDODITHIOUS ACID, AND RELATED SUBSTANCES

A. E. Arbuzov and V. M. Zoroastrova

In previous papers we have studied the action of phosphorous trichloride on simple glycols in presence of pyridine or of dimethylaniline [1], e.g.:



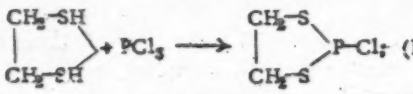
The chlorido ester obtained reacts with alcohols in presence of pyridine to give the corresponding mixed esters of phosphorous acid. In the literature there are described sulfur compounds of analogous structure containing an arsenic [2] or antimony [3] atom, which may be prepared by the action of arsenic trichloride or antimony trichloride on 1,2-ethanedithiol:

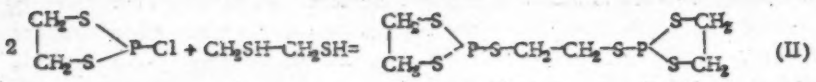


We have not been able to find any data concerning the synthesis of the phosphorous analog in the literature.

We considered it to be of interest in relation to the development of the study of the properties of mixed alkyl cyclic esters of phosphorous acid to synthesize the corresponding thio analogs and to compare their properties with those of the oxygen derivatives. By the action of phosphorus trichloride on ethanedithiol in dry ether we have isolated two reaction products — a liquid and a crystalline solid.

The liquid product was found to be the expected ethylene phosphorochloridodithioite (I), a colorless liquid that fumes strongly in air and has the following constants: b.p. 102-103°/10 mm; d_0^{20} 1.5297; n_D^{20} 1.6700; calculated MR_D 38.79; found MR_D 38.91. The solid product (II), m.p. 130°, was found to be the product of the action of three molecules of ethanedithiol on phosphorus trichloride, and resulted, evidently, from the action of ethanedithiol on the chlorido ester that had been formed:





The formation of an analogous product has been observed in the careful hydrolysis of the chlorido ester obtained by the action of 1,2-ethanedithiol on arsenic trichloride [2].

The chlorido ester I reacts with methanol in presence of pyridine with formation of a methyl ester (OCH_3 in place of Cl). Such alkyl cyclic esters may be prepared also by the action of Menshutkin acid chlorides on 1,2-ethanedithiol. Thus, by the action of ethyl phosphorodichloridite on ethanedithiol in presence of pyridine, the mixed ethyl ester was formed (OC_2H_5 in place of Cl).

Ethylene O-methyl phosphorodithioite is a liquid having the following constants: b.p. 97-98°/7.5 mm; d_4^{20} 1.3426; n_D^{20} 1.6200; calculated MR_D 40.30; found MR_D 40.33. The corresponding O-ethyl ester has the following constants: b.p. 98-99°/6 mm; d_4^{20} 1.2629; n_D^{20} 1.5922; calculated MR_D 44.90; found MR_D 45.09.

The cyclic thioesters obtained have the properties of tervalent phosphorus derivatives and give crystalline complex compounds with cuprous halides. They readily hydrolyze in air.

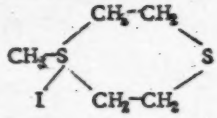
One of the most interesting properties of trialkyl esters of phosphorous acid is their conversion into quinquevalent phosphorous derivatives under the action of alkyl halides. In the case of alkyl cyclic esters of phosphorous acid, the conversion from tervalent to quinquevalent phosphorous may occur, as we have found previously, either with rupture of the cyclic system, or without rupture.

In the case of the thio-derivatives, the course of the reaction may be complicated, as was shown by Kabachnik, Divinsky, and Sidorenko [4], by the occurrence of the addition of alkyl halide not to phosphorous, but to sulfur, with subsequent splitting-off of a thioether and formation of the corresponding phosphorous halide derivative. The experiments that we have performed on the action of ethyl iodide on O-ethyl ethylene phosphorodithioite and on the action of triphenylmethyl bromide on ethylene O-methyl phosphorodithioite have shown that the reaction is complex, and we have not yet succeeded in sorting out the reaction products.

By the action of ethyl iodide on O-ethyl ethylene phosphorodithioite at 80-90° we obtained:

1) A product, b.p. 172-174°/4 mm, corresponding according to analysis to an isomerization product. However, the very high boiling point of the substance compels us to refrain from ascribing to it any definite structure, as an isomer of ethylene hydrogen phosphite.

2) A crystalline substance, m.p. 111-112°, which was found to be p-dithiane, confirmed by conversion into the monomethiodide:



m.p. 173-175°

3) The main bulk of reaction product, which was a transparent semisolid undistillable mass.

On hydrolysis of the substance of b.p. 172-174°/4 mm with 15% HCl at 170°, dithiane, m.p. 111°, and a liquid product, acid in nature and giving a barium salt, were isolated. The hydrolysis was accompanied by the separation of hydrogen sulfide. The action of methyl iodide on ethylene O-methyl phosphorodithioite in a sealed tube at 90° resulted, when the tube was opened, in a violent explosion. When the O-methyl or O-ethyl compounds were treated with triphenylmethyl bromide, the same crystalline product, m.p. 221-222°, was isolated in both cases. In its analysis it corresponds closely to the product that would be formed by addition of triphenylmethyl bromide to the phosphorous ester and subsequent splitting-off of methyl or ethyl bromide. However, hydrolysis of the product by means of hydrochloric acid did not yield triphenylmethylphosphonic acid, which would have indicated addition of triphenylmethyl bromide at phosphorous; nor did it give triphenylmethanol or triphenylmethanethiol, which might have been formed if the initial addition of triphenylmethyl bromide had occurred at sulfur. It was found possible to isolate only triphenylmethane from the reaction products.

Formation of triphenylmethane was observed by A. E. Arbuzov and B. A. Arbuzov [5] in the hydrolysis of Boyd's acid chloride with hydrochloric acid in sealed tubes in presence of ethanol. Separate experiments showed that formation of triphenylmethanol preceded formation of triphenylmethane. We have shown by specially designed experiments that under the conditions of the hydrolysis by hydrochloric acid of the product formed by the action of triphenylmethyl bromide on O-alkyl ethylene phosphorodithioite, i.e. in presence of the hydrogen sulfide formed in this reaction, triphenylmetnanol is reduced to triphenylmethane.

Apart from experiments on the action of phosphorous trichloride and of Menshutkin's acid chloride on ethanedithiol, we have carried out trials on the action of phosphorous trichloride on ethylenediamine with the aim of preparing the corresponding cyclic phosphorous derivatives. Both phosphorous trichloride and Menshutkin's acid chloride react with anhydrous ethylenediamine, and crystalline ethylenediamine hydrochloride is precipitated, but we did not succeed in isolating the reaction product.

EXPERIMENTAL

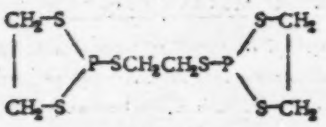
1. Action of Phosphorous Trichloride on Ethanedithiol

Freshly distilled phosphorous trichloride (65.6 g: 1 mole per mole of ethanedithiol) was added to ethanedithiol (45 g; b.p. 146° [6]) dissolved in dry ether (250 ml). When the whole of the phosphorous trichloride had been added, the reaction mixture was heated on the water-bath at 50° for 20 min. A crystalline precipitate (16.3 g) was formed. The liquid part was vacuum-distilled from an Arbuzov flask. A substance

(50.5 g; 66.5%), b.p. 102-103°/10 mm, corresponding in analysis to the required chlorido ester, was obtained. Colorless liquid, fumes strongly in air; d_4^{20} 1.5297; n_D^{20} 1.6700; found MR_D 38.91; calculated MR_D 38.79.

Found %: P 19.93; Cl 21.67; S 40.22
$C_2H_4S_2PCl$. Calculated %: P 19.55; Cl 22.35; S 40.42

After being recrystallized twice from dry benzene, the crystalline precipitate melted at 130°. It corresponded in analysis to the reaction product from 2 mol. phosphorous trichloride and 3 mol. ethanedithiol:



Found %: P 18.41; S 56.99
$C_6H_{12}S_6P_2$. Calculated %: P 18.31; S 56.90

A Rast molecular weight determination gave the following result:

Found: M 350
$C_6H_{12}S_6P_2$. Calculated: M 338.5

2. Action of Menshutkin's Acid Chloride on Ethanedithiol

Ethyl phosphorodichloridite (39.02 g) was added dropwise to an ethereal solution of a mixture of ethanedithiol (25 g) and pyridine (41.95 g) (cooling with snow). After separation of pyridine hydrochloride, the liquid products were vacuum-fractionated. A product (27.5 g, 57.3%), b.p. 98-99°/5 mm, was separated; d_4^{20} 1.2629; n_D^{20} 1.5922; found MR_D 45.09; calculated MR_D 44.90; Found %: P 18.17; 18.24; $C_4H_9S_2PO$. Calculated %: P 18.42.

The product is a colorless liquid having a characteristic unpleasant odor reminiscent of the odors of cyclic esters of phosphorous acid and of mercaptans. It reacts violently with concentrated nitric acid, giving bursts of flame. It reacts with cuprous chloride with formation of a crystalline product, m.p. 122-124°, which rapidly decomposes in air. The product of reaction with CuI melts at 134°; it also is unstable in air.

3. Action of Methanol on Ethylene Phosphorochloridodithioite

Ethylene phosphorochloridodithioite (16 g) was added dropwise to a solution of absolute methanol (3.24 g) and pyridine (8 g) in dry ether (150 ml). The reaction mixture was cooled with snow. The pyridine hydrochloride that separated was filtered off through a Schott funnel. The filtrate, after removal of solvent, was vacuum-distilled. A product (9.18 g, 59%), b.p. 97-98°/7.5 mm, was obtained: d_4^{20} 1.3426; n_D^{20} 1.5200; found MR_D 40.33; calculated MR_D 40.30. Found %: P 20.26; S 42.10; $C_3H_7S_2PO$. Calculated %: P 20.11; S 41.66.

The product is a liquid of unpleasant odor. On being cooled in snow it crystallizes to a white mass that rapidly melts at ordinary temperature. It reacts with cuprous iodide with evolution of much heat. Like the ethyl ester, it bursts into flame on being brought into contact with concentrated nitric acid.

4. Action of Ethyl Iodide on O-Ethyl Ethylene Phosphorodithioite

O-Ethyl ethylene phosphorodithioite (12 g) and ethyl iodide (11 g) were sealed in a tube and heated at 80-90° for 3 hrs. At the end of the reaction, ethyl iodide (10 g) was distilled off, and the remaining reaction products were vacuum-distilled. During distillation partial decomposition occurred, and in addition to liquid products a crystalline material came over, and this was separated mechanically. The latter was found on investigation to be dithiane (m.p. 111-112°); on being heated with methyl iodide it yielded a crystalline product corresponding in m.p. (173-174°) to the product of the addition of methyl iodide to dithiane. A liquid product (3 g; 25%), when regarded as an isomerization product), b.p. 172-174°/4 mm, was separated. A large part of the reaction products remained in the distillation flask as a dirty-pink rubberlike mass.

The fraction of b.p. 172-174°/4 mm had d_4^{20} 1.2648; n_D^{20} 1.6375.

Found %: P 18.96; S 39.95
$C_4H_9S_2PO$. Calculated %: P 18.42; S 38.13

Hydrolysis of the Product. The substance of b.p. 172-174°/4 mm (1.8 g) was heated in a sealed tube with 15% HCl (20 ml) at 165-170° for 3 hrs. The tube was opened, and the contents were found to be heterogeneous; they comprised liquid, a half-solid white mass, and some crystals; a large amount of hydrogen sulfide

was evolved. After being distilled, the crystalline product melted at 111°; it was dithiane. Some more dithiane was separated by distillation from the semisolid mass. The liquid was heated on the water bath until hydrogen chloride had been completely removed. By boiling of the residue with barium carbonate, the barium salt was obtained.

Found %: Ba 39.37
$C_2H_5PS_2OBa$. Calculated %: Ba 49.40

5. Action of Methyl Iodide on Ethylene O-Methyl Phosphorodithioite

Ethylene O-methyl phosphorodithioite (6.4 g) and methyl iodide (6 g) were sealed in a tube and allowed to stand at room temperature. After standing overnight, the contents of the tube had become turbid. After the mixture had been heated at 30° for 0.5 hrs, it acquired the color of iodine. When an attempt was made to open the tube it exploded in the hands and the whole of the contents were thrown out with great force.

6. The Reaction between Ethylene O-Methyl Phosphorodithioite and Triphenylmethyl Bromide

Triphenylmethyl bromide (2.2 g) was dissolved by heat in dry benzene (5 ml). To the cooled solution ethylene O-methyl phosphorodithioite (1.05 g = 1 mol) was added. At first a homogeneous solution was formed, but after 2-3 min a precipitate began to appear; it had a pale dirty-pink color. The reaction was accompanied by scarcely appreciable evolution of heat. The product (2.5 g) was filtered off. After being recrystallized twice from dioxane and benzene it melted at 221-222°.

Found %: P 8.42; S 17.60
$C_{21}H_{19}PS_2O$. Calculated %: P 8.10; S 16.80

Rast molecular weight determination.
Found: M 373.1
$C_{21}H_{19}PS_2O$. Calculated: M 382.4

Hydrolysis of the Product of m.p. 221-222°. The product (0.8 g) and 15% HCl (15 ml) were heated in a sealed tube at 200° for 3 hrs. When the tube was opened, an odor of hydrogen sulfide was observed. Some crystals (0.2 g), much contaminated with resin, were isolated; they melted, after recrystallization from alcohol, at 92-93°. M.p. in admixture with pure triphenylmethane was also 92-93°. The liquid, which was of a brown color, was evaporated almost to dryness on the water bath. Some sort of product remained in the dish in the form of a brown incrustation.

7. Action of Triphenylmethyl Bromide on O-Ethyl Ethylene Phosphorodithioite

O-Ethyl ethylene phosphorodithioite (1.68 g) and triphenylmethyl bromide (3.23 g) were heated in benzene solution for 20 min at the boil. When the mixture was cooled, a precipitate (3.7 g) appeared. After recrystallization from benzene and gasoline, the product melted at 221-222°. It melted without depression when mixed with the previous product.

Expt. 1. Triphenylmethylphosphonic acid (0.25 g) and 15% HCl (12 ml) saturated with hydrogen sulfide were sealed in a tube and heated at 200-220° for 5 hrs. Triphenylmethylphosphonic acid was recovered unchanged (m.p. 280°).

Expt. 2. The experiment was carried out with the same amounts of the substances, but in presence of ethylene glycol (0.08 g). The same conditions of heating were observed. Triphenylmethylphosphonic acid was obtained in admixture with resinous contamination.

Expt. 3. A mixture of triphenylmethanol (0.52 g) and 15% HCl (25 ml) saturated with hydrogen sulfide was heated in a sealed tube at 200-220° for 5 hrs. The tube was cooled, and a crystalline product (0.3 g) was filtered off. M.p. after being recrystallized twice from absolute alcohol: 92-93°. In admixture with triphenylmethane it gave no depression (92-93°). In addition to triphenylmethane, some yellow needles, m.p. 119°, were obtained in very small quantity.

Expt. 4. An analogous experiment was carried out with the same amounts of triphenylmethanol and hydrochloric acid saturated with hydrogen sulfide, but ethylene glycol (1.12 g) was added. After purification of the reaction products, triphenylmethane (0.4 g, m.p. 92-93°) was obtained. The m.p. in admixture with pure triphenyl-

methane was again 92-93°. In addition to triphenylmethane, a small amount of crystals that melted at 117-119° to a yellow liquid were obtained.

SUMMARY

1. By the action of phosphorous trichloride on 1,2-ethanedithiol a cyclic ester of phosphorochloridodithious acid has been prepared.

2. Mixed O-alkyl ethylene esters of phosphorodithious acid have been prepared both by the action of an alcohol on ethylene phosphorochloridodithioite in presence of pyridine, and also by the action of Menshutkin's acid chloride on ethanedithiol.

3. The O-alkyl ethylene phosphorodithioites obtained react with alkyl halides (methyl iodide, triphenylmethyl bromide). The structures of the products obtained have not been established.

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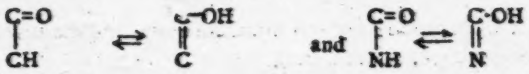
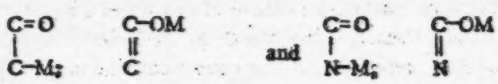
THE QUESTION OF THE TAUTOMERISM OF ISATIN

A. E. Arbuzov and M. Sh. Bastanova

For more than 80 years, right up to the present time, chemists have been concerned with the phenomena of tautomerism. The compounds that have been the subject of tautomerism studies belong to a great variety of classes of organic and inorganic compounds. The most detailed study has been made of compounds that show keto-enol and lactam-lactim tautomerism. The mobile parts of the molecules of such compounds may be represented as follows:

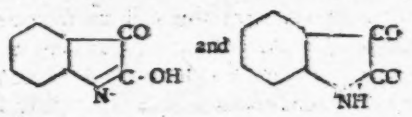


Correspondingly, the metal derivatives may be represented as:



One of the most characteristic properties of tautomeric compounds is their ability to give, according to the conditions, derivatives that differ in structure.

Classical examples of compounds showing lactam-lactim tautomerism are isatin, carbostyril, and derivatives of these compounds.* Thus, already in 1882 Baeyer and Oekonomides [5] showed that when the sodium derivative of isatin was methylated in aqueous solution with dimethyl sulfate a methylisatin (m.p. 134°) was obtained in good yield. This compound is not hydrolyzed by alkalis, but gives "N-methylisatin-sodium". The same N-methylisatin is obtained when methyl iodide and the sodium salt of isatin in the dry state are heated together at 100° in a sealed tube. If, however, methyl iodide is allowed to react with the dry silver derivative of isatin in ether at ordinary temperature, O-methylisatin (m.p. 101-102°) is obtained. This O-derivative is hydrolyzed by aqueous alkalis, giving isatin and methanol. As yet, isatin itself has been obtained in one form only, but as it forms two series of derivatives, regarded as O- and N-derivatives, two forms may be assigned to it:



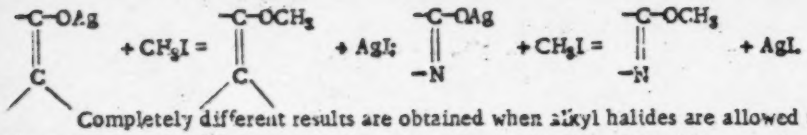
(I) (II)

The question of the structure of tautomeric compounds is closely bound up with the question of the structure of their metal derivatives. In the literature there is a great deal of material on this question [1,5,6,7,8], and it is evident from this that the question of the structure of the salts of tautomeric compounds, in particular of the salts of isatin, is much more complicated than might have been supposed. Some investigators consider the salts to have the N-structure, others consider them to have the O-structure. It is found that the material available in the literature does not admit of definite conclusions: some investigators consider that the metal derivatives may exist in two isomeric forms, and of these, some consider the metal to be fixed in position, while others assume tautomerism; the majority of chemists, however, consider them to have the enol structure, whatever the nature of the metal may be.

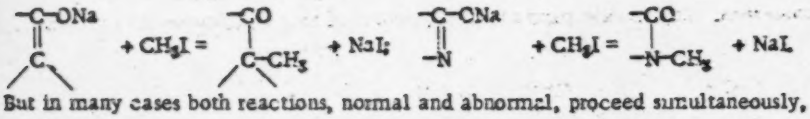
If such is the position it will be found necessary to distinguish two types of replacement reaction. In the first type products of direct replacement of the metal by a radical are obtained: such reactions have been called "normal". In the second type the radical takes up a position other than that of the metal, and we have an "abnormal" reaction.

* See p. 446

From the enormous amount of experimental material that has been accumulated it has been possible to derive a number of guiding rules. Thus, it may be assumed that in an overwhelming majority of cases silver derivatives of tautomeric compounds on reacting with alkyl halides yield normal reaction products, i.e. the corresponding O-ethers. In this case the reactions may be represented by the following schemes:



Completely different results are obtained when alkyl halides are allowed to react with alkali derivatives. The entering radical then usually occupies a place other than that of the metal, i.e. C- or N-derivatives are obtained. In this case the reaction schemes will take the following forms:



But in many cases both reactions, normal and abnormal, proceed simultaneously, and the relative amounts of the products depend on reaction conditions (temperature, solvent, etc).

No particular difficulty is met in the explanation of normal reactions, for they are normal replacement reactions, but the explanation of abnormal reactions, particularly those of isatin and carbostyril derivatives, has turned out to be a question that is far from simple. Usually either the O- or the N-derivative (most frequently the N-derivative) is obtained, the course of the reaction depending on the conditions, the nature of the metal, etc.; in some cases both derivatives are obtained simultaneously in variable relative amounts.

The formation of N-methylisatin may evidently be represented in two different ways: we may either acknowledge that the sodium derivative has the lactam form, i.e. that the sodium is on the nitrogen, or assume formation of the O-derivative and its subsequent conversion into the N-derivative.

Thus, if we regard the salts of tautomeric compounds as O-salts, we must assume that certain changes occur during the reaction. These changes may occur either before the reaction of the metal derivative of the tautomeric compound with alkyl halide, under suitable reaction conditions, or during reaction with alkyl halide with splitting-off of the metal halide. It follows that the tautomerism of isatin (and carbostyril) derivatives, while constituting an extremely interesting field of tautomerism, cannot at present form the basis of definite conclusions on this question.

To elucidate the matter by purely chemical means will be obviously very difficult, and further work of this sort on questions of tautomerism must proceed in the direction of the accumulation and extension of the experimental material in this field; by study of a greater number of reactions, taking into account the effects due to the size and structure of the radical of the substance reacting with the tautomeric compound, to the nature of the halogen, to the temperature conditions, to the solvent, etc., and also by carrying out investigations based on physicochemical data. The study of absorption spectra has not enabled the structure of isatin to be determined, i.e. it has not shown whether the hydrogen is bound to N or to O [7,9,10,11].

Up to the present the only isatin derivative that has been shown to have the O-form is the O-methyl ether prepared by Baeyer. In 1939 A. E. Arbuzov [2] prepared a triphenylmethyl derivative of isatin, "O-triphenylmethylisatin", by the action of triphenylmethyl bromide and chloride on the silver and sodium salts of isatin. In all four reactions A. E. Arbuzov isolated a triphenylmethylisatin of m.p. 232-233°; since it was readily hydrolyzed by heating in a caustic soda solution on the water-bath, it was assigned the O-structure. Later, the two triphenylmethylisatins, which differ in color, were investigated spectrographically, and it was shown the yellow and the red form have identical absorption spectra. It was concluded that the red and the yellow forms of the triphenylmethyl derivative of isatin are different crystalline modifications [3]. The formation of a red and of a yellow form of triphenylmethylisatin was pointed out also in a thesis by Alimov [4].

In the present communication the results are given of a study of double decomposition reactions between salts (Na and Ag) of isatin and certain halogen compounds, including halogen-substituted ethers.

There are indications in the literature that the preparation of isatin ethers is associated with certain difficulties and is not always successful; one of the conditions for their preparation is the absolute purity of the materials used, beginning with isatin itself. The isatin used in this work was carefully purified. After recrystallization from glacial acetic acid it had a stable melting point of 198°. The starting compounds were the sodium and silver salts of isatin prepared according to the directions given in the literature.

A study was made of the reaction of salts of isatin with the following halogen compounds: benzyl bromide, benzyl chloride, (α-bromo-p-xylene, allyl iodide,) and (α-bromo-α,α-diphenyl-p-tolyl)-triphenylmethane. (α-Bromo-α,α-diphenyl-p-tolyl)-triphenylmethane was prepared, following Chichibabin, by bromination in the light of (α,α-diphenyl-p-tolyl)-triphenylmethane in carbon disulfide solution [12]. The remaining halogen compounds were prepared by the usual methods. Also, the following halogen-substituted ethers were used: bromomethyl methyl, chloromethyl methyl, bromomethyl ethyl, chloromethyl ethyl, bromomethyl propyl, and chlormethyl propyl; these were prepared from the corresponding alcohols by saturation with halogen halide in presence of formaldehyde or trioxymethylene [13]. All the starting materials were taken for reaction in the freshly prepared condition. The reactions were carried out in dry ether or in benzene, either at room temperature or at the boiling point of the solvent.

By the action of benzyl bromide or chloride on the silver or sodium salt of isatin, a benzyl isatin of m.p. 131° was obtained in all cases; it had the form of glistening sharp red needles. Benzylisatin was found to be a stable compound, not hydrolyzed by heating with dilute acids and caustic alkalis. Experiments on its isomerization in presence of benzyl bromide and on the action of methyl iodide did not give positive results.

By the action of α-bromo-p-xylene on the silver or sodium salt of isatin, (p-tolylmethyl)isatin, m.p. 141-142°, was isolated in all cases in the form of glistening long red crystals. Attempts to hydrolyze (p-tolymethyl) isatin in a solution of caustic potash or of hydrochloric acid were not successful, the (p-tolylmethyl)-isatin remaining unchanged.

By the action of bromo- or chloro-methyl methyl ether on the silver or sodium salt of isatin, the methoxymethyl ether of isatin, m.p. 90-91°, was formed in all cases. By the action of bromo- or chloro-methyl ethyl ether on the silver or sodium salt of isatin, the ethoxymethyl ether of isatin, m.p. 85-86°, was formed in all cases. Bromo- or chloro-methyl propyl ether similarly yielded the propoxymethyl ether, m.p. 79-80°, in all cases.

The rate of reaction varied as follows: the mixed methyl ethers reacted mosted readily, then the propyl ethers, and finally the ethyl ethers. All the alkoxymethyl ethers of isatin are orange substances, readily soluble in ether and in benzene.

Hydrolysis of the methoxy-, ethoxy-, and propoxy-methyl ethers of isatin by the action of hot solutions of alkalis or acids led to formation of isatin (in almost theoretical yield), formaldehyde, and the corresponding alcohols. The readiness with which the alkoxymethyl ethers of isatin undergo hydrolysis appears to indicate that they may be regarded as orthoisomers.

When methyl iodide or benzyl bromide was heated with isatin methoxymethyl ether, high-melting products were obtained.

In addition to a study of the above reactions, a study of reactions with the halides of high-molecular-weight and unsaturated radicals was of interest. For this purpose (α-bromo-α,α-diphenyl-p-tolyl)-triphenylmethane and allyl iodide were taken. As a result of the reactions carried out, canary-yellow diphenyl (α,α,α-triphenyl-p-tolyl)-methylisatin, m.p. 250-252°, was isolated. An attempt to hydrolyze this compound with dilute alkali did not give positive results.

By the action of allyl iodide on the silver salt of isatin a resinlike product was obtained from which it was difficult to isolate anything. By the action of allyl iodide on the sodium salt a scarlet substance was isolated; this had the odor that is characteristic of substances containing the allyl radical, and it melted at 86-87°.

EXPERIMENTAL

PREPARATION OF N-BENZYLISATIN

Action of Benzyl Bromide on the Silver Salt of Isatin

Expt. 1. The silver salt of isatin (1.5 g) was added to a solution of benzyl bromide (1.09 g) in dry benzene (10 ml). The flask was stoppered and allowed to stand in a dark place at room temperature, the contents being agitated by shaking from time to time. After 1-2 hrs a noticeable change in the color of the salt had occurred. On the tenth day the precipitate was filtered off, washed and subjected to extraction with dry benzene. The weight was 1.04 g (calculated AgBr: 1.1 g).

From the main benzene solution, after removal of part of the solvent in a vacuum desiccator, there appeared a precipitate of benzylisatin, m.p. 118-124°. M.p. after recrystallization from ether: 130-131°.

Analysis of substance having m.p. 130-131°

Found %: N 5.25

$C_{18}H_{11}O_2N$. Calculated %: N 5.90

Action of Benzyl Chloride on the Silver Salt of Isatin

Expt. 2. The silver salt of isatin (1.3 g) was added to a solution of benzyl chloride (0.81 g) in dry benzene (10 ml). The experimental conditions were similar to those of the previous experiment. The reaction went very slowly. After two months almost the whole of the bordeaux-red silver derivative had been converted into white silver chloride. From the benzene solution, after removal of silver chloride and part of the solvent, there precipitated a yellowish-red substance, m.p. 119-125°, which after two recrystallizations from benzene melted at 130-131°.

Action of Benzyl Bromide on the Sodium Salt of Isatin

Expt. 3. The sodium salt of isatin (1.69 g) was added to a solution of benzyl bromide (1.71 g) in dry ether (20 ml). The reaction was carried out in a sealed tube at 160° for 2 hrs. When the tube was opened, there was an odor of benzyl bromide. Sodium bromide was removed, and part of the solvent was driven off under reduced pressure, when yellowish-red precipitate came down, m.p. 131-131.5° after two recrystallizations from ether. The residue after evaporation of the whole of the ether was recrystallized from aqueous alcohol and had m.p. 131-131.5° (1.05 g, 44.3%).

Action of Benzyl Chloride on the Sodium Salt of Isatin

Expt. 4. The sodium salt of isatin (1.69 g) was added to a solution of benzyl chloride (1.23 g) in dry ether (20 ml). The reaction was carried out in a sealed tube. The tube was heated for 2 hrs at 140° and 2 hrs at 160°. The result was similar to that of the previous experiment, but a greater amount of unchanged salt was left. From the ethereal solution after removal of part of the solvent a precipitate was formed of a substance of m.p. 126-127.5°, and this melted after two recrystallizations from alcohol at 131-131.5° (0.85 g altogether, 35.8%).

Melting-point determinations on mixtures of the substances obtained in the preceding experiments gave full coincidence: m.p. of mixture of substances from Expt. 1 and 4, 131-131.5°; from Expt. 2 and 4, 131-131.5°; from Expt. 3 and 4, 131-131.5°.

PREPARATION OF (p-TOLYLMETHYL)-ISATIN

Action of α-Bromo-p-xylene on the Silver Salt of Isatin

The silver salt of isatin (1.27 g) was added to a solution of α-bromo-p-xylene (0.93 g) in dry benzene (15 ml). The flask was stoppered and allowed to stand in a dark place. From time to time the contents were agitated. The reaction began very soon, but proceeded slowly. After 48 hrs the products were treated as in Expt. 1. From the benzene solution a substance m.p. 138-139° was isolated. M.p. after recrystallization from alcohol: 141° (0.8 g, 70%).

Analysis of substance, m.p. 141°

Found %: N 5.08

$C_{16}H_{13}O_2N$. Calculated %: N 5.57

Action of α-Bromo-p-xylene on the Sodium Salt of Isatin

The sodium salt of isatin (1.68 g) was added to a solution of α-bromo-p-xylene (1.84 g) in dry ether (10 ml). The reaction was carried out in a sealed tube for 2 hrs at 100°. From time to time heating was interrupted and the contents of the tube were mixed. The contents of the tube were filtered, and the precipitate was washed with ether. A dirty greasy red substance smelling of α-bromo-p-xylene separated from the ethereal solution after evaporation of ether; it was recrystallized three times from alcohol and had m.p. 140.5-141° after the first recrystallization, and 142° after the second and third recrystallizations (1.15 g, 45%). M.p. of mixture of substances obtained in this and preceding experiments: 140-141.5°.

Benzylisatin and (p-tolylmethyl)-isatin crystallized out in all of the experiments as glistening well-formed sharp yellowish-red needles. Concentrated ether and benzene solutions of these are red, but they become yellow on dilution.

PREPARATION OF THE METHOXYMETHYL ETHER OF ISATIN

Alkoxymethyl ethers of isatin were prepared as follows. A round-bottomed flask was connected through a two-way adapter to a reflux condenser carrying a thermometer, which was lowered into the center of the reaction mixture, and to a dropping funnel, from which a solution of the halogen-substituted ether was added dropwise. At the end of the reaction the precipitate of halide salt was filtered off and extracted in a Soxhlet with the same solvent. The alkoxymethyl ethers of isatin, which after recrystallization had stable melting points, were isolated from the main solution and from the solution obtained after extraction. Melting-point determinations on mixtures of the alkoxymethyl ethers obtained by the use of bromine- and chlorine-substituted ethers and of silver and sodium isatin salts gave identical results. The alkoxymethyl ethers obtained from the solution from the extraction, especially when the solvents used had not been freshly dehydrated and distilled, contained small amounts of isatin, evidently owing to partial hydrolysis of the main substance present. In every experiment the yields of alkoxymethyl ether and of metal halide were determined.

All the alkoxymethyl ethers of isatin formed yellowish-orange crystals of good solubility in ether and in benzene. In solution and as finely divided powder they are yellow.

Action of Bromomethyl Methyl Ether on the Silver Salt of Isatin

A solution of bromomethyl methyl ether (1.13 g) in ether (15 ml) was added gradually to the silver salt of isatin (2.54 g) in freshly distilled ether (10 ml). The reaction started immediately, heat being evolved (30-35°). 30 min. after the whole of the bordeaux-red silver salt of isatin had been converted into yellow silver bromide, the precipitate of halide salt was separated and treated as indicated above.

From the ether solution an orange substance was isolated; after recrystallization from dry ether: 1.12 g, 63.9%; m.p. 90-91°. From the ether solution from a 4 hr extraction of the silver bromide, 0.32 g of red substance, m.p. 186-191°, was obtained, i.e. 0.4 g calculated as methoxymethyl isatin; consequently, the total yield of the methoxymethyl ether of isatin may be considered to be 1.5 g (87.2%).

Analysis of substance, m.p. 90-91°

Found %: N 6.72

$C_{10}H_9O_3N$. Calculated %: N 7.32

Action of Chloromethyl Methyl Ether on the Silver Salt of Isatin

Chloromethyl methyl ether (0.71 g) in dry ether (20 ml) was added to the silver salt of isatin (2.54 g). Reaction commenced immediately after addition of chloromethyl methyl ether, and proceeded with evolution of heat. After 30 min the precipitate of silver chloride was filtered off and extracted. An orange substance, m.p. 90-95°, (0.54 g, 28.1%) was isolated from the ether solution; its melting point remained unchanged after recrystallization from dry ether.

From the ether solution from the extraction (with 150 ml) of the silver chloride, a reddish-orange substance, m.p. 88-90° was precipitated; in the melting-point test a small amount of substance remained unmelted, but disappeared somewhat above 100°. A second extraction yielded 0.12 g of a substance of m.p. 84-106°, and a third yielded 0.15 g of a substance of m.p. 196-198° and of a red color, i.e. isatin. The total yield of methoxymethyl ether, taking this isatin into account, was 1.28 g (67.0%).

Action of Bromomethyl Methyl Ether on the Sodium Salt of Isatin

Bromomethyl methyl ether (1.2 g) in dry ether (30 ml) was added to the sodium salt of isatin (1.69 g). Appreciable reaction was noticeable after about 10 min, when slight warming occurred (23-25°). When the whole of the black sodium salt of isatin had been converted into a light-colored precipitate of sodium bromide, the latter was filtered off, washed, and extracted with ether. From the main ether solution and from the solution from the extraction of NaBr, orange crystals, m.p. 90-90.5°, (1.6 g, 87.3%) were isolated.

Action of Chloromethyl Methyl Ether on the Sodium Salt of Isatin

Chloromethyl methyl ether (0.81 g) in dry ether (20 ml) was added to the sodium salt of isatin (1.69 g). The reaction mixture was warmed on the water-bath. When the sodium salt of isatin had been converted into a white precipitate of sodium chloride, the latter was separated from the solution. From the main ether solution and from the solution from the extraction of NaCl, orange crystals, m.p. 90-91°, (1.55 g, 81.1%) were precipitated.

A melting point determination on a mixture of the substances obtained in all four reactions indicated complete identity: the mixture melted at 90.5-91.5°.

PREPARATION OF THE ETHOXYMETHYL ETHER OF ISATIN

Action of Bromomethyl Ethyl Ether on the Silver Salt of Isatin

Bromomethyl ethyl ether (1.4 g) in dry ether (25 ml) was added to the silver salt of isatin (2.54 g). Reaction with evolution of heat (the reaction mixture boiled) rapidly set in. The flask was heated for 30 min on the water-bath, and the precipitate of silver bromide was then separated and extracted with ether. The ethereal solutions yielded an orange substance, m.p. 85-86° (1.4 g, 68.3%).

It is of interest to note that during the crystallization a reddish ring of crystals formed in the higher regions; these melted at a considerably higher temperature than the main product. This, evidently, was isatin, formed by the partial hydrolysis of its ethoxyethyl ether.

Action of Chloromethyl Ethyl Ether on the Silver Salt of Isatin

Chloromethyl ethyl ether (0.68 g) in dry ether (20 ml) was added to the silver salt of isatin (1.9 g). The flask was heated in a bath of glycerol at 40-43° for one hour. The silver chloride was then separated. The ethereal solutions yielded a bright-orange substance having a golden reflex, m.p. 84-86°. (1.26 g, 82.2%). Its color was richer than that of the methoxymethyl ether. On recrystallization from ether a small amount (0.05 g) of a red undissolved substance remained; it melted at 196-198° and appeared to be isatin.

Analysis of substance, m.p. 85-86°

Found %: N 6.67

$C_{11}H_{11}O_3N$. Calculated %: N 6.83

Action of Bromomethyl Ethyl Ether on the Sodium Salt of Isatin

Bromomethyl ethyl ether (0.9 g) in dry ether (20 ml) was added to the sodium salt of isatin (1.1 g). Reaction proceeded at room temperature, but was slow. After an hour the flask was warmed on the water bath for 10 min to complete reaction. The sodium bromide was separated and washed several times with dry ether. The ethereal solutions yielded bright-orange crystals, m.p. 85-86° (0.51 g, 38.2%). A further 0.65 g of material was extracted from the mother liquor, and this, after being recrystallized twice from ether, melted at the same temperature. When the substance is left open to the air it becomes red, evidently owing to hydrolysis of the ethoxymethyl ether to isatin.

Action of Chloromethyl Ethyl Ether on the Sodium Salt of Isatin

Chloromethyl ethyl ether (0.62 g) in dry ether (20 ml) was added to the sodium salt of isatin (1.0 g), and the mixture was heated on the water-bath for 2 hrs. From the ethereal solution bright-orange crystals were separated (m.p. 85-85.5°; 0.36 g, 30%). A further 0.45 g of material was extracted from the mother liquor, and this, after being recrystallized twice from ether, had the same melting point. Mixed melting points on the ethoxymethyl ethers obtained by the four reactions described above all had the same value of 85-85.5°.

PREPARATION OF THE PROPOXYMETHYL ETHER OF ISATIN

Action of Bromomethyl Propyl Ether on the Silver Salt of Isatin

Bromomethyl propyl ether (0.93 g) in dry ether (50 ml) was added gradually to the silver salt of isatin (1.55 g). Reaction set in rapidly and proceeded with evolution of heat. At the end of the reaction the flask was heated for 10 minon the water bath. The main solution was partially distilled from a Wurtz flask. Red crystals (0.05 g, m.p. 192-198°) came out of the remaining solution on cooling. A reddish residue remained in the distillation flask (0.2 g, m.p. 164-172°); this, after recrystallization from glacial acetic acid, melted at 198-200°. It was undepressed in melting point when mixed with isatin.

The main solution after removal of isatin was partially distilled off under vacuum, when light-orange crystals having a golden reflex and of m.p. 77-78° came down. After recrystallization from ether the melting point was considerably higher, rising to 99-100°.

Analysis of Substance of m.p. 77-78°

Found % N 6.22

$C_{12}H_{15}O_3N$. Calculated % N 6.39

Action of Chloromethyl Propyl Ether on the Silver Salt of Isatin

A solution of chloromethyl propyl ether (0.66 g) in dry ether (20 ml) was added gradually to the silver salt of isatin (1.56 g). Reaction set in at once with evolution of heat (temperature of reaction mixture, 33°). After 30 min the flask was heated on a water bath for 10 min. From the ether solution an orange substance of m.p. 78-80° was isolated.

Analysis of substance of m.p. 78-80°

Found % N 6.12

$C_{12}H_{15}O_3N$. Calculated % N 6.39

Action of Bromomethyl Propyl Ether on the Sodium Salt of Isatin

A solution of bromomethyl propyl ether (2.3 g) in dry ether (30 ml) was added to the sodium salt of isatin (2.6 g). The reaction soon began, but proceeded slowly, so the mixture was heated to the boil on the bath ($\frac{1}{2}$ hr). From the ether solution an orange substance (2.1 g, 62.5%; m.p. 78-80°) was isolated.

Action of Chloromethyl Propyl Ether on the Sodium Salt of Isatin

A solution of chloromethyl propyl ether (1.1 g) in dry ether (20 ml) was added to the sodium salt of isatin (1.69 g). The reaction went more slowly than the previous one, and the reaction mixture was therefore heated for an hour. An orange substance crystallized out from the ether solution. It was recrystallized twice from dry ether (1.66 g, 75.8%; m.p. 79-80°).

Analysis of substance of m.p. 79-80°

Found % N 6.30

$C_{12}H_{15}O_3N$. Calculated % N 6.39

M.p. determinations on mixtures of the propoxymethyl ethers obtained in the four reactions gave 78-80°.

Hydrolysis of Benzylisatin

Benzylisatin (0.2 g) was heated in a sealed tube with 10% HCl or 10% KOH at 140-150° for one hour. After neutralization and ether extraction, benzylisatin, m.p. 131-131.5°, was recovered unchanged.

Hydrolysis of (p-Tolylmethyl)Isatin

Expt. 1. (p-Tolylmethyl)isatin (0.1 g) and 10% HCl (5 ml) were heated together in a sealed tube at 130-140° for 1 hr and at 140-150° for 1 hr. The substance that precipitated when the mixture was cool was filtered off, washed, and dried (0.8 g, m.p. 138.5-140°).

Expt. 2. (p-Tolylmethyl)isatin (0.13 g) and 10% KOH (5 ml) were heated together in a sealed tube under the same temperature conditions as in Expt. 1. All the substance was in solution. When the solution was neutralized with hydrochloric acid, an orange substance was precipitated; it was washed and dried (0.1 g, m.p. 139-140°.

The substances obtained in Expt. 1 and 2 were recrystallized together from alcohol and had m.p. 140.5-142°. In admixture with (p-tolylmethyl)isatin obtained from the sodium salt this melted at 141-142°.

Hydrolysis of Diphenyl (α, α, α-Triphenyl-p-Tolyl)-Methylisatin

The substance (0.2 g) was heated with 10% KOH (20 ml) for 1 hr. From the solution, after neutralization and ether extraction, a substance of m.p. 246-247° was isolated.

Hydrolysis of Isatin Methoxymethyl Ether in Presence of Acid

The methoxymethyl ether of isatin (0.2 g) was heated in a sealed tube with a dilute (3%) solution of hydrochloric acid at 145-150° for 2 hrs. The tube was opened, and the acid was back-titrated. From the solution isatin, m.p. 193-196°, was isolated; it was recrystallized from glacial acetic acid (0.08 g, 55%; m.p. 199-200°).

Hydrolysis of Isatin Methoxymethyl Ether in Presence of Caustic Alkali

Isatin methoxymethyl ether of m.p. 90-90.5° (0.15 g) was heated in a flask with a dilute solution of KOH (20 ml, 0.13 g KOH) for half an hour. The solution was then neutralized with hydrochloric acid and partially distilled off. Tests on the distillate for aldehyde (Schiff's reagent and ammoniacal silver nitrate) gave positive results. The remaining solution was extracted repeatedly with ether, and the extract, on evaporating down, yielded a precipitate of isatin, m.p. 194-196° rising to 199-200° after recrystallization from glacial acetic acid (0.08 g, 76.6%). The m.p. was undepressed when an admixture of pure isatin was made.

Hydrolysis of Isatin Ethoxymethyl Ether

Isatin ethoxymethyl ether of m.p. 85° (0.7 g) was heated in a flask fitted with reflux condenser with dilute KOH solution (30 ml, 0.6 g KOH) for 1 hour. The solution was then neutralized with hydrochloric acid. A part of the solution was distilled off, and qualitative tests were made for formaldehyde and ethanol. The solution gave a magenta color with Schiff's reagent and a silver mirror with ammoniacal silver nitrate; with iodine dissolved in a solution of potassium iodide and caustic potash it gave a yellow precipitate of iodoform.

The remaining solution was repeatedly extracted with ether, and from the ethereal solution, after evaporation of some of the ether, a precipitate of isatin was formed in almost quantitative yield. The melting point, after recrystallization from glacial acetic acid, was 200°; in admixture with pure isatin it melted at 199-200°.

Hydrolysis of Isatin Propoxymethyl Ether

Isatin propoxymethyl ether of m.p. 79-80° was heated in a flask under reflux with dilute sulfuric acid (40 ml) for 1 hour. The acid was then back-titrated and, as in the above-described reactions, aldehyde was detected in the solution by a qualitative reaction. The remaining solution was extracted with ether, and isatin was isolated as before, m.p. after recrystallization from glacial acetic acid 199-200° (0.32 g, 80%).

Action of Alkyl Halides on Isatin Ethers

Action of Methyl Iodide and of Benzyl Bromide on Benzylisatin

Expt. 1. Benzylisatin of m.p. 131° (0.14 g) and methyl iodide (0.4 g) were heated together in a sealed tube at 120-140° for 3 hours. After heating and cooling, the liquid had the same level. Methyl iodide was driven off under reduced pressure. The substance remaining in the tube melted at 130-131°, and in admixture with the starting material it melted at 130.5°.

Expt. 2. Some of the same benzylisatin (0.1 g) was heated with benzyl bromide for 2 hours at 100-155° and for 2 hours at 160-170°. The contents of the tube were cooled and filtered under suction, and the residue was washed repeatedly with ether. 0.08 g of material of m.p. 130-130.5° was recovered. The mixed m.p. was 130-131°.

Action of Benzyl Bromide on Isatin Methoxymethyl Ether

Isatin methoxymethyl ether (0.3 g) was heated in a sealed tube with benzyl bromide (1.5 g). Heating was for 2 hours at 150-160° and 2 hours at 175-185°. When the tube had cooled, fine crystals came down and the volume was found to be somewhat reduced (1.5-2 mm). The solution had become more reddish in color. Opening of the tube revealed no excess pressure. The precipitated crystals were filtered off and washed several times with ether (0.09 g of crystals). In the melting-point test, the substance began to change its color somewhat — from reddish yellow to grayish brown — but did melt when heated to 292°. From the benzyl bromide solution a further 0.04 g of material came down; it was washed with ether and tested for melting point, but did not melt up to 292° and gradually became darker in color as the temperature rose above 300°.

Action of Benzyl Bromide on Isatin Ethoxymethyl Ether

Isatin ethoxymethyl ether (0.11 g) and benzyl bromide (0.38 g) were heated together in a sealed tube for 2 hours at 160-170°. The solution became more yellowish in color. The benzyl bromide was distilled off under reduced pressure, and a yellow substance (0.6 g) was isolated. It was washed several times with ether and then tested for melting point. At above 240° it began to go reddish, above 260° it began to go brown, and finally it became almost black and melted (270-272°).

SUMMARY

1. By the action of the bromomethyl and chloromethyl ethers of methyl, ethyl, and propyl alcohols on the sodium and silver derivatives of isatin, the corresponding isatin ethers have been prepared: isatin methoxymethyl ether of m.p. 90-91°, isatin ethoxymethyl ether of m.p. 85-86°, and isatin propoxymethyl ether of m.p. 79-80°.

2. All the derivatives obtained were readily hydrolyzed.

3. The hydrolysis products of the methoxy-, ethoxy-, and propoxy-methyl ethers of isatin were isatin (obtained in almost quantitative yield), formaldehyde, and the corresponding alcohols.

4. By the action on the sodium and silver derivatives of isatin of (α-bromo-α,α-dipheryl-p-tolyl)-triphenylmethane, of benzyl bromide and chloride, and of α-bromo-p-xylene there were obtained diphenyl-(α, α,α-triphenyl-p-tolyl)-methylisatin of m.p. 250-252°, benzylisatin of m.p. 131°, and (p-tolylmethyl)-isatin of m.p. 141-142°.

5. Attempts to hydrolyze the substances of m.p. 131°, 141-142°, and 250-252° did not give satisfactory results; the substances were recovered unchanged. The question of their structures remains an open one.

6. When the methoxymethyl and ethoxymethyl derivatives of isatin are heated with methyl iodide or with benzyl bromide, high-melting products are obtained.

7. Benzylisatin remains unchanged in presence of methyl iodide or of benzyl bromide.

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SYNTHESIS AND PROPERTIES OF α-ALKOXYETHYL ESTERS OF UNSATURATED CARBOXYLIC ACIDS ("ACYLALS")

M. F. Shostakovsky, N. A. Gershtein, Ya. L. Raskin, and L. E. Ostroumova

Acrylic acids and their derivatives, which have a conjugated system of double bonds $>C=C-C=O$, readily enter into various reactions, particularly polymerization and copolymerization reactions. Polymers of acrylates, and particularly of methacrylates and also of acrylic acids, are valuable materials (films, plastics, Plexiglas, Crystalite, etc.), which have been widely applied in industry. The method of synthesis of this class of compound was sketched out by Favorsky [1] already in 1894 in terms of the reaction that he discovered between distributed acetylene hydrocarbons and hypochlorous acid:

$$CH_3C\equiv C-CH_3 + 2HOCl \longrightarrow CH_3CCl_2-CO-CH_3 \xrightarrow[K_2CO_3]{10\%} CH_2=\underset{CH_3}{\overset{|}{C}}-COOH$$

This reaction was studied on the basis of many examples, and Favorsky [2] writes as follows about it: "Thus, the reaction in which unsaturated acids are formed by the action of a 10 % solution of potassium carbonate on α,α-dichloro ketones may be considered, on the basis of facts already given, to be a general reaction, and in view of this it may be expressed by the following series of equations:

$$R'-CO-CHCl_2 + H_2O \longrightarrow R''=CH-COOH + 2HCl. \qquad (I)$$

$$\begin{array}{l} R' \\ | \\ CCl_2 \\ | \\ C=O \\ | \\ CH_3 \end{array} + H_2O \longrightarrow \begin{array}{l} R''=C-COOH \\ \qquad\quad | \\ \qquad\quad CH_3 \end{array} + \begin{array}{l} CH_2=C-COOH \\ \qquad\quad | \\ \qquad\quad R' \end{array} + 2HCl. \qquad (II)$$

However, the development of industry based on acrylic acids was delayed by the absence of simple and accessible methods for the synthesis of acrylic esters. Thus, up to 1927 methyl acrylate was obtained by a very complex route:

$$CH_2=CH-CH_2OH + Br_2 \longrightarrow CH_2Br-CH_2OH \xrightarrow{O} CH_2Br-CHBr-COOH \xrightarrow{ROH} CH_2Br-CHBrCOOR \xrightarrow{Zn}$$

$$\longrightarrow CH_2=CH-COOR\ (R=CH_3).$$

Later, an economically sounder method for the preparation of methylacrylate via 2-chloroethanol was developed:

$$HOCH_2-CH_2Cl \xrightarrow{NaCN} HOCH_2-CH_2CN \xrightarrow[H_2SO_4]{CH_3OH} CH_2=CH-COOCH_3.$$

As well as by this method, methyl acrylate is now prepared in industry by a pyrolysis method from lactic acid:

$$CH_3CH-COOH \longrightarrow CH_3CH-COOCH_3 \xrightarrow{475\text{-}650^\circ} CH_2=CH-COO-CH_3$$

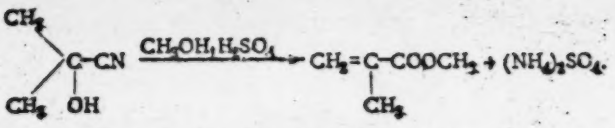
$$\qquad\quad | \qquad\qquad\quad |$$

$$\qquad OH \qquad\quad OCOCH_3$$

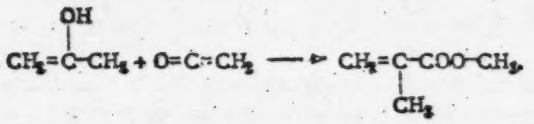
Still wider application has been accorded the methacrylates, which polymerize more readily and give products having more desirable properties; practical interest in them is therefore high. However, the synthesis of esters of methacrylic acid, particularly the methyl ester, also requires complex methods [3,4]:

$$\begin{array}{l} CH_3-C-COOCH_3 \\ \qquad\quad | \\ \qquad CH_2 \quad OH \end{array} \xrightarrow{PCl_5} \begin{array}{l} CH_3 \\ | \\ CH_2-C-C-O-CH_3 \\ \qquad\quad | \quad \| \\ \qquad\quad Cl \quad O \end{array} \longrightarrow CH_2=\underset{CH_3}{\overset{|}{C}}-COOCH_3$$

which does not differ in principle from Favorsky's method:



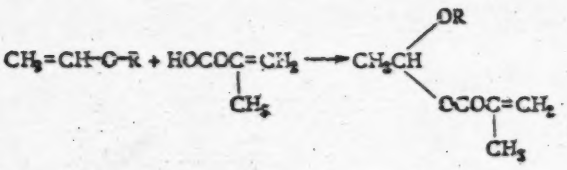
Quite recently a method has been described for the preparation of methacrylic esters by the condensation of ketones with ketenes in presence of sulfanilic acid derivatives as catalysts [5]:



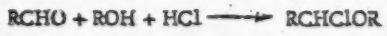
The higher esters of acrylic acids are synthesized by alcoholysis of the methyl esters. It is natural, therefore, that the interest of chemists in the preparation of more and more new acrylic acid derivatives continues unabated.

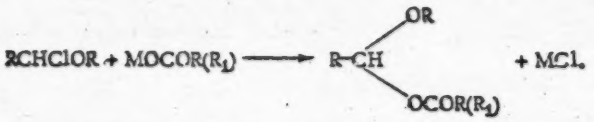
The vinyl ethers, which also are very reactive compounds, have recently become industrial products, thanks mainly to the work of Favorsky and Shostakovsky. That is why the combination of vinyl ethers and acrylic acids opens up the prospect of preparing new, practical, valuable products and is enriching chemistry with new, extremely interesting compounds.

The aim of the present investigation was to prepare from vinyl ethers and methacrylic acid a series of new ester-like substances of an unsaturated nature, viz. the acylals, and to study their properties.

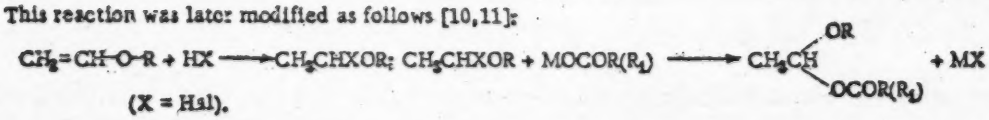


In the previous communication [6] a method was described for the synthesis of 1-alkoxyethyl esters by the addition of carboxylic acids to vinyl ethers. This reaction has greatly simplified the preparation of acylals. The previously known methods for the preparation of acylals via unstable α-halo ethers and salts of carboxylic acids are more complex [7-9]:



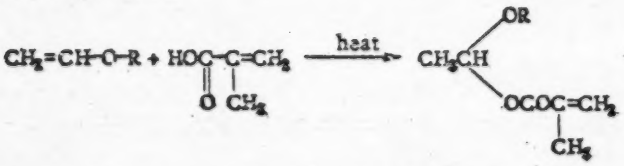


This reaction was later modified as follows [10,11]:



(X = Hal).

For the synthesis of unsaturated acylals we have made use of the method of direct addition of methacrylic acid to vinyl ethers:



It was found that this reaction proceeds fairly smoothly and gives unsaturated acylals in 65-80% yield. A study was made also of the effect of the addition of catalysts (mineral acids) on the yield, but the expected increase in yield was not obtained.

In the present communication we describe the synthesis and properties of α-cyclohexyloxy-, α-benzyloxy-, and α-phenoxy-ethyl methacrylates. The starting substances were methacrylic acid and the vinyl ethers of cyclohexanol, benzyl alcohol, and phenol. In a number of patents [12] on the vinylation of hydroxy compounds, the above vinyl ethers are included among those listed, but the constants and yields of the first two are practically passed over.

We synthesized these two ethers by the method of Favorsky and Shostakovsky [13], slightly modified. The yields of vinyl ether were 68-69%. The acylals prepared from them are liquids having a characteristic ethereal odor; they polymerize when heated in presence of peroxide catalysts. The structural peculiarities of these acylals, which contain in their molecules a number of conjugated double bonds, are manifested in their molecular refractions by an increased exaltation. Our results are given in Table 1.

Hydrolytic splitting of these acylals proceeds as follows:

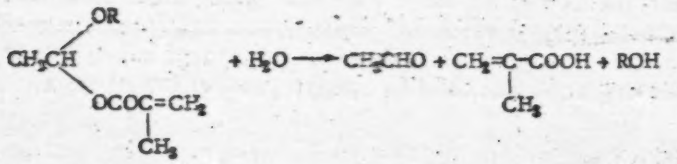
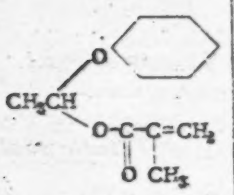
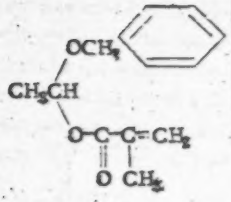
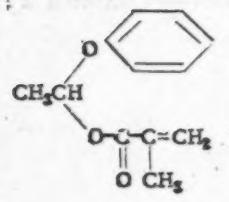


TABLE 1

Molecular Refractions of Acylals

Compound	MP.		Difference
	Found	Calculated	
	59.02	58.246	0.774
	62.58	61.463	1.117
	57.75	56.845	0.905

However, the rate at which this decomposition occurs depends to an appreciable extent on the structure of the radical R. When R is an aliphatic radical, hydrolysis is brought about fairly rapidly in the cold by means of 2-5% solutions of mineral acids (simple shaking for 2-3 min). When R is C_6H_{11} (cyclohexyl), hydrolysis under the same conditions requires 25-30 min. When R is $C_6H_5CH_2$ about an hour is required, and when R is C_6H_5 heating at 100° for 3-5 hrs is required. Thus, with respect to the effect of the radical R on the rate of acid hydrolysis of the acylals studied, the following series may be written:

$$\text{Alkyl} > C_6H_{11} > C_6H_5CH_2 > C_6H_5.$$

The densities of acylals having a radical R containing an aromatic nucleus are greater than unity.

EXPERIMENTAL

Synthesis of Cyclohexyl Vinyl Ether $CH_2=CH-O-C_6H_{11}$ (I)

Cyclohexanol (100 g) and solid caustic potash (10 g) were loaded into a 500-ml rotating autoclave and heated with acetylene, which was admitted in portions under a pressure of 14-18 atm, to 148-150°. At this temperature heating was continued for 1.5-2 hrs for each portion of acetylene. At the end of the reaction a mobile brown liquid (115.5 g) was obtained. The autoclave was washed with ether. The ether extracts were added to the main product, which had been diluted with ether. The ethereal solution of the product was washed several times with water in a separating funnel. All the wash waters were shaken, in their turns, 2-3 times with ether. All the ether extracts were dried with calcined potassium carbonate and filtered. The solvent was removed, and the residue vacuum-fractionated. Cyclohexyl vinyl ether (87.5 g, 68.6%), b.p. 52-54°/23 mm was obtained. Similarly, from 210 g of cyclohexanol and 20 g of caustic potash under the same conditions 182 g of cyclohexyl vinyl ether was obtained (69.5% of cyclohexanol). Cyclohexyl vinyl ether is a colorless, transparent, very mobile liquid having an

ethereal odor; b.p. 52-54° at 23 mm; b.p. 63° at 37 mm; b.p. 47.2-47.5° at 15 mm; n_D^{20} 1.4547; d_4^{20} 0.888; found MR_D 38.50; calculated for $C_8H_{14}O$ MR_D 38.12. B.p. 147-148° [14].

Found %: C 76.30; H 11.33
$C_8H_{14}O$. Calculated %: C 76.19; H 11.11

The cyclohexyl vinyl ether was hydrolyzed by means of a 2% solution of sulfuric acid. The acetaldehyde formed was determined quantitatively by Ripper's method [15]

Found %: AcH 98.11 (of theoretical)

Synthesis of Benzyl Vinyl Ether $CH_2=CH-OCH_2-C_6H_5$ (II)

The conditions for the synthesis of benzyl vinyl ether were the same as for the synthesis of cyclohexyl vinyl ether. From 110 g of benzyl alcohol (freshly distilled) and 11 g of caustic potash, with introduction of acetylene under a pressure of 18 atm, 84.7 g (62%) was obtained. Similarly, from 80 g of benzyl alcohol and 8 g of caustic potash 67.5 g (68%) of benzyl vinyl ether was obtained. B.p. 81.5° at 22 mm; b.p. 82.5° at 24 mm; n_D^{20} 1.5185; d_4^{20} 0.9711; found MR_D 41.87; calculated for $C_9H_{10}O$ MR_D 41.337. [16]; b.p. 183-184°; n_D^{20} 1.5160; d_4^{20} 0.9710.

Found %: C 80.40; H 7.63
$C_9H_{10}O$. Calculated %: C 80.55; H 7.51
Found %: AcH 98.24 (of theoretical)

SYNTHESIS OF ACYLALS

1. Synthesis of 1-Benzyloxyethyl Methacrylate $CH_3CH(OCH_2C_6H_5)-O-CO-C(CH_3)=CH_2$

Expt. 1 (without catalyst). A mixture of freshly distilled methacrylic acid (10.8 g, 0.12 mole), b.p. 160-161°, n_D^{20} 1.4113 and 20 g (0.15 mole) having the above-indicated constants were heated in a sealed tube on a boiling water bath for 4.5-5 hrs. The reaction products were fractionally distilled in a stream of nitrogen, which was passed through an alkaline solution of pyrogallol, through sulfuric acid, and over solid caustic potash or soda. A substance was obtained (12.9 g, 78.5%) of b.p. 82-82.2°/14 mm.

Expt. 2 (in presence of H_2SO_4 as catalyst). Freshly distilled methacrylic acid (5 g) and benzyl vinyl ether (12.7 g) were introduced into a three-necked flask fitted with reflux condenser and mechanical, mercury-sealed stirrer; with constant stirring sulfuric acid (0.05% on methacrylic acid taken) was added as a 2% alcoholic solution. There was a slow spontaneous rise in the reaction temperature from 17 to 50° in 1 hr 15 min, and the temperature was then maintained at this level for 3 hrs. The reaction mass was left overnight and then vacuum-distilled in a stream of nitrogen in presence of antioxidants. The yield of pure substance, b.p. 83.7-84°/15 mm, was 9.9 g (77.6%).

1-Benzyloxyethyl methacrylate is a colorless liquid having an ethereal, camphor-like odor; b.p. 82-82.2° at 14 mm; b.p. 83.7-84° at 15 mm; n_D^{20} 1.5008; d_4^{20} 1.0367; found MR_D 62.58; calculated $C_{13}H_{16}O_3$ MR_D 61.463.

Found %: C 70.48; H 7.00
$C_{13}H_{16}O_3$. Calculated %: C 70.92; H 7.33

Found by hydrolysis with 2% sulfuric acid: AcH 98.01% of theoretical.

2. Synthesis of 1-Cyclohexyloxyethyl Methacrylate $CH_3CH(OC_6H_{11})OCOC(CH_3)=CH_2$

Expt. 1 (without catalyst). By proceeding under the conditions of the previous synthesis from 8.6 g (0.1 mole) of the freshly distilled acid and 20.6 g (0.16 mole) of cyclohexyl vinyl ether, heated in a sealed tube for 5 hrs, we obtained 16.5 g (77.8%) of the required acylal, b.p. 114-115°/20 mm.

Expt. 2 (in presence of H_2SO_4 as catalyst). By proceeding under the conditions of the previous synthesis from 7 g of freshly distilled methacrylic acid and 19.4 g of cyclohexyl vinyl ether in presence of 0.05% of sulfuric acid, we obtained 13.65 g (79.1%) of acylal, b.p. 112-112.5°/19 mm.

1-Cyclohexyloxyethyl methacrylate is a colorless, transparent liquid having a characteristic ethereal odor; b.p. 112-112.5° at 19 mm; b.p. 113.5-114° at 20 mm; b.p. 115-115.2° at 20 mm; n_D^{20} 1.4560; d_4^{20} 0.9776; found MR_D 59.02, calculated $C_{13}H_{24}O_3$ MR_D 58.246.

Found %: C 67.84; H 9.50
$C_{13}H_{24}O_3$. Calculated %: C 67.88; H 9.50
Found %: AcH 98.07

3. Synthesis of 1-Phenoxyethyl Methacrylate $CH_3CH(OC_6H_5)-O-CO-C(CH_3)=CH_2$

The synthesis of 1-phenoxyethyl methacrylate was carried out by means of heat in presence of catalysts. The addition of methacrylic acid to phenyl vinyl ether requires more severe conditions (higher temperature and more prolonged heating), and these lead to polymerization of the phenoxyethyl methacrylate formed.

It follows from the results given in Table 2 that with an excess of vinyl ether of up to 30% and with various periods of heating the yield of acylal remains practically constant. The distillation of phenoxyethyl methacrylate was carried out in a stream of nitrogen in presence of 0.5% of toluylenediamine. 1-Phenoxyethyl methacrylate has the following constants: b.p. 98-99° at 15 mm; b.p. 129-130° at 20 mm; n_D^{25} 1.5030; d_4^{20} 1.0561; found MR_D 57.75; calculated $C_{12}H_{14}O_3$ MR_D 56.845.

Found %: C 70.40; H 7.00
$C_{12}H_{14}O_3$. Calculated %: C 69.85; H 6.84

TABLE 2

Synthesis of Phenoxyethyl Methacrylate

Expt. No.	Ratio of reagents: Ether (mol)	Ratio of reagents: Acid (mol)	Catalyst (mol H_2SO_4 per mol acid)	Max. reaction temp. °C	Duration of heating	Yield of acylal after fractionation (%)
1	1.28	1	$43 \cdot 10^{-5}$	60	1 hr 30 min exothermic reaction and 1 hr further heating at 60°	93.3
2	1.26	1	$43 \cdot 10^{-5}$	60	1 hr 30 min exothermic reaction and 1 hr 30 min further heating at 60°	90.8
3	1.15	1	$43 \cdot 10^{-5}$	70	1 hr 15 min exothermic reaction and 2 hrs 30 min further heating at 70°	92.4

Found by hydrolysis with 5% sulfuric acid: AcH 97.44 % of theoretical.

SUMMARY

1. Unsaturated acylals have been synthesized for the first time from aralkyl vinyl, aryl vinyl, and cyclohexyl vinyl ethers and methacrylic acid.

2. The properties of the acylals obtained have been described.

3. The relation between the rate of hydrolysis of these acylals and the structure of the ether radical has been found, and on its basis radicals have been placed in a series corresponding to a diminishing tendency in the acylals to hydrolysis.

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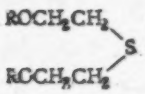
SYNTHESIS OF SULFUR COMPOUNDS BY THE AID OF VINYL ETHERS

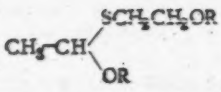
COMMUNICATION 5. SOME NEW α,β- AND β,β'-DIALKOXY DERIVATIVES OF DIETHYL SULFIDES

E. N. Prilezhaeva, E. S. Shapiro, and M. F. Shostakovsky

In the present communication a description is given of the conditions of synthesis and also certain properties of α,β- and β,β'-dialkoxy derivatives of diethyl sulfide obtained from isobutyl vinyl and isoamyl vinyl ethers. The reactions of these ethers have confirmed all the regularities that have been established previously for the addition reaction between gaseous hydrogen sulfide and vinyl ethers in dioxane in presence of HCl as catalyst [1]. The yield of reaction products, a mixture of isomeric dialkoxy derivatives of diethyl sulfide (I, II, III, and IV), is 80-85%.



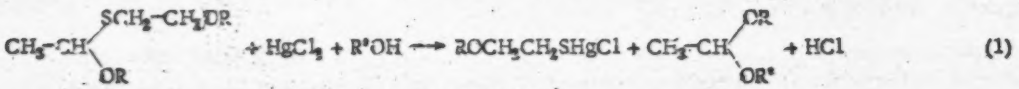
(I), (III)



(II), (IV)

(I), (II) R = iso-C_4H_9 (III), (IV) R = iso-C_5H_{11}

The percentage contents of isomers in this mixture were determined by the aid of the analytical method proposed in the same communication [1]; it is based on the decomposition of sulfides II and IV in presence of an alcoholic solution of mercuric chloride (equation 1).*

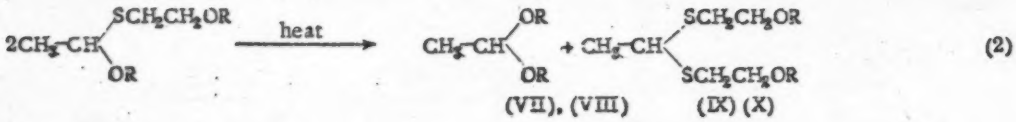


(1)

(V), (VI)

(V) R = iso-C_4H_9 (VI) R = iso-C_5H_{11}

The new representatives of the series of α,β-dialkoxy derivatives of diethyl sulfide, which have a monothioacetal structure, are similar to those described previously [3] and differ greatly in thermal stability and chemical properties from the β,β'-dialkoxydiethyl sulfide series. Thus, prolonged storage, heating, and particularly treatment with acids leads to disproportionation with formation of equimolecular amounts of dialkyl acetals (VII, VIII) and of the corresponding β-β'-alkoxyethyl mercaptals (IX, X) according to equation 2:

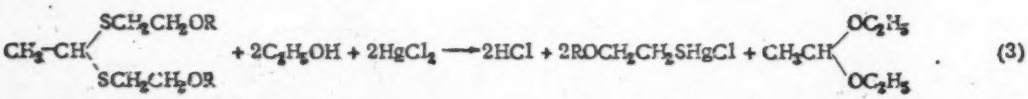


(2)

(VII), (IX) (VIII), (X)

(VII), (IX) R = iso-C_4H_9 (VIII), (X) = iso-C_5H_{11}

Acetaldehyde bis-β-alkoxyethyl mercaptals, like other members of the mercaptal class [4], do not give stable complex salts with mercuric chloride, but react with the latter according to Equation 3 with formation of alkoxyethylmercaptomercury chlorides (V, VI) identical with those obtained from the corresponding sulfides (II, IV) (Equation 1).



(3)

* A similar analytical method was proposed earlier by Holmberg [2] for the quantitative determination of derivatives of β,α'-(methylenedithio)-diacetic acid (bis-(carboxymethyl) mercaptals and mercaptoles).

Thus, new examples have been found that confirm the characteristic chemical behavior of sulfides having alkoxy or alkylmercapto groups on the carbon adjacent to the sulfur atom.

EXPERIMENTAL*

1. Action of Hydrogen Sulfide on Isobutyl Vinyl Ether

a) To 25 g of isobutyl vinyl ether there was added, after a preliminary 15 min passage of hydrogen sulfide through the system, 0.2 ml of 17% catalyst (0.1% by wt of HCl on ether taken). The experiment was carried out under a pressure of hydrogen sulfide at room temperature for 12.5 hr. No appreciable rise in temperature was to be observed. The reaction was then continued for an hour at 43°. After 13.5 hr the increase in weight of the reaction mass was 2 g.

Fractional distillation gave:

Unchanged ether – 4 g
Fraction 1, b.p. 33-34° at 3.5 mm – 0.5 g
Fraction 2, b.p. 100-106° at 2.5 mm – 19.8 g; n_D^{20} 1.4485
Residue, a brown viscous substance – 0.8 g.

Fraction 1 gave a qualitative reaction for mercaptan. Fraction 2 was a mixture of the isomeric sulfides I and II; yield 80.5% of the ether. Amount of α,β-isomer (II) by titration: 55.3; 55.1%.

b) 106 g of isobutyl vinyl ether, 0.1 ml of 26.4% catalyst (0.03% by wt on ether of HCl). The experiment was carried out at 50°. After 3 hrs, very vigorous absorption of hydrogen sulfide began. After 30 hrs the increase in weight was 16.5 g. Fractionation of the product yielded unchanged ether (6.6 g), and the residue was fractionated twice and yielded the following fractions: in the trap (at –75°) 2.7 g, n_D^{23} 1.4078; [illegible]

Fraction 1, 34-37° at 4 mm – 1.8 g; n_D^{23} 1.4120
Fraction 2, 70-100° at 4 mm – 1.9 g; n_D^{23} 1.4430
Fraction 3, 105-113° at 4 mm – 101.4 g; n_D^{21} 1.4505
Fraction 4, 150-160° at 4 mm – 7.5 g; n_D^{23} 1.4691

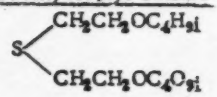
By repeated fractionation of the product collected in the trap and of Fraction 1, diisobutyl acetal (VII) was isolated, and from Fraction 4, bis(2-isobutoxyethyl) mercaptal (IX) was isolated; both substances are disproportionation products from α,β-isobutoxyethyl sulfide (II) and are characterized below in detail. The yield of the sulfide fraction (3) was 87% . Amount of α,β-isomer (II) by titration: 26.7; 26.4 %.

Thus, under conditions of lower acidity the percentage of α,β-isomer in the mixture is reduced, but rise in the reaction temperature is accompanied by increase in the extent of disproportionation of the α,β-sulfide with formation of fractions 1 and 4.

2. Properties of the Isomeric Diisobutoxy Derivatives of Diethyl Sulfide (I and II)

The mixture of disulfides was resolved into the practically pure isomers by vacuum fractionation through a column of 18-20 theoretical plates.

1) β,β'-Dibutoxydiethyl Sulfide



(I)

is a liquid having practically no distinct odor. It is an extremely stable substance; b.p. 124° at 5 mm; 116.2-116.4° at 3.5 mm; n_D^{20} 1.4510, d_4^{20} 0.9126; found MR_D 69.16; calculated MR_D 68.88.

Found %: C 61.48; 61.49; H 11.18; 11.20; S. 13.63; 13.55
$C_{12}H_{26}O_2S$. Calculated %: C 61.49; H 11.18; S 13.68;

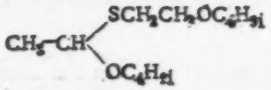
β,β'-Diisobutoxydiethyl sulfide(II) does not give an acid reaction in presence of mercuric chloride, but forms a complex compound with mercuric chloride that crystallizes in large plates: $C_{12}H_{26}O_2S \cdot HgCl_2$, m.p. 47°.

Found %: S 6.20; 6.14
$C_{12}H_{26}O_2S \cdot HgCl_2$. Calculated %: S 6.31

* For details of procedure see Communication 2 [1].

In the literature [5] on α,β'-diisobutoxydiethyl sulfide, i.e., the following constants, which are appreciably different from those cited by us, are given: b.p. 268-272°; n_D^{20} 1.4580; d_4^{20} 0.9216. For the complex compound $i\text{-}C_{12}H_{26}O_2S \cdot HgCl_2$ the obviously erroneous m.p. of 71° is given. This lack of agreement must be attributed to the incomplete purity of the products obtained by the author, who in studying the action of zinc dust on β,β'-chloroethyl sulfide in alcohol obtained a complex mixture of products, which he separated further merely by the method of simple fractionation at ordinary pressure.

2) α,β-Diisobutoxydiethyl Sulfide



(II)

is a colorless liquid having a sharp odor; m.p. 103-105° at 3.5-4 mm; n_D^{20} 1.4486; d_4^{20} 0.9077; found MR_D 69.21; calculated MR_D 68.88.

Found %: C 61.41; 61.33; H 11.23; 12.15; S 13.77; 13.48
$C_{12}H_{26}O_2S$. Calculated %: C 61.49; H 11.18; S 13.68

(a) Reaction of an alcoholic solution of mercuric chloride with the sulfide II gives, in accordance with Equation 1, quantitative separation of hydrochloric acid and the alkoxyethylmercaptomercuric chloride.

Found: α,β-isomer (II) 97.7; 97.9 %.

The precipitated white β-isobutoxyethylmercaptomercuric chloride was obtained by repeated recrystallization from large amounts of boiling alcohol in the form of white tabular crystals, m.p. 144°.

Found %: Cl 9.50; 9.39; S 8.68; 8.60
$C_6H_{13}OSHgCl$. Calculated %: Cl 9.60; S 8.68

(b) Disproportionation of α,β-diisobutoxydiethyl sulfide (II). The sulfide II (11.5 g) and 27% HCl (1 ml) in dioxane were heated in a sealed tube on a boiling water bath for 12 hrs.

After two distillations, the following fractions were obtained:

Fraction 1, 42-43° at 3.5 mm – 3.8 g; n_D^{20} 1.4046
Fraction 2, 50-103° at 3.5 mm – 0.9 g; n_D^{20} 1.4580
Fraction 3, 155-159° at 3 mm – 5.7 g; n_D^{20} 1.4791

Fraction 1, after treatment with metallic sodium and repeated fractionation was found to be diisobutyl acetal (VII), b.p. 42-43° at 3.5 mm; b.p. 170° at 760 mm; n_D^{20} 1.4022; d_4^{20} 0.8180; found MR_D 51.90; calculated MR_D 51.67. [6] m.p. 168-170°; sp.gr. 0.816 at 22°. The bisulfite method of analysis [7] (with addition of H_2SO_4) gave for acetal: 99.1; 99.3%.

Fraction 3 was found to be bis(β-isobutoxyethyl) mercaptal (IX) and had the following constants after repeated fractionation: b.p. 152-154° at 2.7 mm; n_D^{20} 1.4798; d_4^{20} 0.9685; found MR_D 86.36; calculated MR_D 86.04.

Found %: C 56.84; 57.01; H 10.30; 10.34; S 21.84; 21.55
$C_{16}H_{32}O_2S_2$. Calculated %: C 57.09; H 10.27; S 21.77

(c) Action of mercuric chloride on bis(β-isobutoxyethyl) mercaptal (IX) (equation 3). A 20% alcoholic solution of mercuric chloride (6 ml) was added to the mercaptal IX (0.55 g). A finely crystalline white precipitate of β-isobutoxyethylmercaptomercuric chloride (V) formed quickly. The precipitate, after being washed with cold alcohol and dried in a vacuum desiccator, weighed 1.5 g (against theoretical 1.4 g). After being recrystallized twice from hot alcohol, the precipitate melted at 144° and was undepressed in m.p. when mixed with β-isobutoxyethylmercaptomercuric chloride (obtained from the α,β-sulfide II).

3. Action of Hydrogen Sulfide on Isoamyl Vinyl Ether

(a) 55 g of the ether, 0.2 ml of catalyst (0.098% by wt. on the ether of HCl). The experiment was carried out for 7 hrs at room temperature and 12 hrs at 43-45°. The total increase in weight of the reaction mass was 8 g. There were obtained on distillation:

Fraction 1, 30-34° at 5-4.5 mm – 1.1 g; n_D^{20} 1.4168

Fraction 2, 49-50° at 4 mm – 0.9 g; n_D^{20} 1.4458

Fraction 3, 75-125° at 4 mm – 0.8 g; n_D^{20} 1.4573

Fraction 4, 127-134° at 3 mm – 49.7 g; n_D^{20} 1.4560

Fraction 5, 160-175° at 3 mm – 3.8 g; n_D^{20} 1.4670

Amount of α,β-isomer (IV) in mixture: 33.7; 33.7 %. Yield of fraction 4 (mixture of the sulfides) 83.8%.

(b) 35 g of the ether, 0.5 ml of catalyst (0.39% by wt of HCl). The experiment was carried out at room temperature (19°). After 5.5 hr the temperature of the reaction mixture reached 26°, and absorption of hydrogen sulfide started suddenly. The experiment lasted for 13 hrs. Increase in weight, 4.5 g. The residue after the unchanged ether (2.4 g) had been driven off was fractionated:

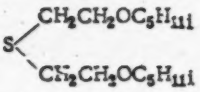
Fraction 1, 35-45° at 2-2.2 mm – 1.2 g
Fraction 2, 90-122° at 2 mm – 1.4 g
Fraction 3, 125-134° at 2 mm – 30.5 g; n_D^{20} 1.4530

Amount of α,β-isomer (IV) in the mixture: 61.1; 61.2%. Yield of fraction 3 (mixture of the sulfides) 81.9%.

4. Properties of the Isomeric Diisoamyloxy Derivatives of Diethyl Sulfide (III) and (IV)

Separation of the mixture of isomers was carried out, as in the previous case, by vacuum distillation through an efficient column. As these substances have high viscosities, the fractionating process was rendered difficult, and the α,β-isomer (IV) was consequently isolated in an insufficiently pure form.

1) β,β'-Diisoamyloxydiethyl Sulfide



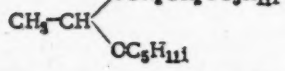
(III)

does not give an acid reaction on addition of an alcoholic solution of mercuric chloride; b.p. 130.2-131° at 2.6-2.8 mm; n_D^{20} 1.4552; d_4^{20} 0.9090; found MR_D 78.4; calculated MR_D 78.1.

Found %: C 64.49; 64.39; H 11.61; 11.65; S 12.44; 12.25
$C_{14}H_{30}O_2S$. Calculated %: C 64.06; H 11.53; S 12.22

Gives a liquid complex compound with mercuric chloride. For this sulfide the literature gives b.p. 191-192 at 33 mm [5].

2) α,β-Diisoamyloxydiethyl Sulfide



(IV)

b.p. 102-104° at 1.7 mm; n_D^{23} 1.4533; d_4^{20} 0.9052; found MR_D 78.41; calculated MR_D 78.11.

Found %: C 63.37; 63.77; H 11.47; 11.43; S 11.99; 12.10
$C_{14}H_{30}O_2S$. Calculated %: C 64.05; H 11.53; S 12.22

The sulfide (IV) decomposes when it is treated with an alcoholic solution of mercuric chloride with formation of β-isoamyloxyethylmercaptomercuric chloride and with separation of HCl (in accordance with Equation 1).

Content found of α,β-isomer (IV) 91.9; 91.4%.

After being recrystallized twice from hot alcohol, the mercury derivative VI melted at 124.5-125°.

Found %: Cl 9.13; 9.28; S 8.33; 8.11
$C_7H_{15}OSHgCl$. Calculated %: Cl 9.25; S 8.36

In order to bring about its disproportionation, the sulfide(IV)(10 g) was heated in presence of 27.6% HCl (1 ml) in dioxane for 12 hrs on a boiling water bath. The tube was opened and the reaction product diluted with ether. It was washed four times with water in a separating funnel (to remove acid) and then dried. The ether was removed, and the reaction product was vacuum-fractionated:

Fraction 1, 28-29° at 3 mm – 1.6 g
Fraction 2, 66-69° at 3 mm – 1.6 g
Fraction 3, 160-170° at 3 mm – 6.1 g

Isoamyl alcohol was isolated from Fraction 1. From Fraction 2, after a second fractionation, there was separated diisoamyl acetal (VIII); b.p. 66-67° at 3 mm; n_D^{20} 1.4158; d_4^{20} 0.8358; found MR_D 60.72; calculated MR_D 60.90. [8]: b.p. 210.8° (760 mm); sp.gr. 0.8347 at 15°. Fraction 3 was bis(β-isoamyloxyethyl) mercaptal (X). After two fractionations it had the following constants: b.p. 172-175°/3.2 mm; n_D^{20} 1.4800; d_4^{20} 0.9569; found MR_D 95.76; calculated MR_D 95.31.

Found %: C 59.65; 59.49; H 10.72; 10.63; S 19.72; 19.78
$C_{16}H_{34}O_2S_2$. Calculated %: C 59.57; H 10.63; S 19.88

From the ββ'-diisoamyloxydiethylmercaptal(X)obtained by the action of an alcoholic solution of mercuric chloride, there was obtained, in accordance with equation 3, isoamyloxyethylmercaptomercuric chloride (VI). After two recrystallizations it melted at 125° and was undepressed in m.p. when mixed with isoamyloxyethylmercaptomercuric chloride obtained from the sulfide(IV).

SUMMARY

1. It has been shown that addition of hydrogen sulfide to isobutyl vinyl and isoamyl vinyl ethers in dioxane in presence of HCl under conditions similar to those previously described for other vinyl ethers again results in the formation of mixtures of α,β- and β,β'-dialkoxy derivatives of diethyl sulfide.

2. A study has been made of certain chemical reactions of new homologs in the series of dialkoxydiethyl sulfides and β,β'-dialkoxydiethylmercaptals.

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SYNTHESIS OF THE VINYL ETHERS OF HIGHER FATTY ALCOHOLS

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The Favorsky-Shostakovsky method [1] for the vinylation of alcohols has received general recognition and wide application in laboratory practice and in industrial production. The great interest aroused by vinyl ethers has brought the question of the vinylation of higher fatty alcohols into prominence. The sporadic data concerning a few alkyl vinyl ethers that is to be found in the foreign patent literature and the isolated facts in our own literature do not present a complete picture of these compounds.

In order to make a study of the general and individual properties of these ethers, the vinylation of the following fatty alcohols was undertaken: hexyl, cyclohexyl, heptyl, octyl, iso-octyl, nonyl, and decyl (see Table 1).

TABLE 1

Characteristics of Alcohols Used

Name and Formula	B.p. °C/760 mm	n_D^{20}
Hexyl alcohol $C_6H_{13}OH$	157	1.4181
Heptyl alcohol $C_7H_{15}OH$	175-176	1.4228
Octyl alcohol $C_8H_{17}OH$	196	1.4290
Iso-octyl alcohol $C_6H_{13}CHCH_2$	179-180	1.4275
Nonyl alcohol $C_9H_{19}OH$	214-215	1.4363
Decyl alcohol $C_{10}H_{21}OH$	231	1.4370
Cyclohexyl $C_6H_{12}OH$	160.7	1.4645

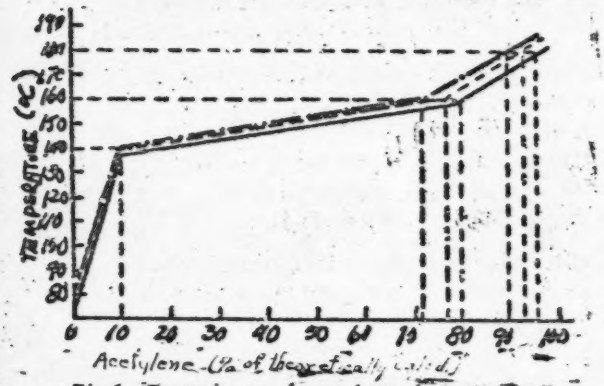

Fig.1. Dependence of acetylene absorption on temperature: ——— nonyl and decyl alcohols; ——— octyl and iso-octyl alcohols; — — — hexyl, heptyl, and cyclohexyl alcohols

It was found that vinylation of higher fatty alcohols exhibits certain peculiarities. The vinylation process proceeds more slowly than for the C_1–C_5 alcohols. At 140-160°, only 72-80% of the theoretically necessary acetylene is absorbed (Fig.1). When the temperature is then raised to 180°, 90-96% of acetylene is absorbed, depending on the complexity of the alcohol used. Further raising of the temperature causes secondary reactions.

The rate of vinylation depends on the initial pressure of acetylene (Fig.2). For an initial pressure of 17-18 atm the time required for vinylation of 3 mole of alcohol is 2.5 hrs less than for 12-13 atm initial pressure. Hexyl alcohol vinylates more rapidly than octyl alcohol. Iso- and cyclic alcohols vinylate somewhat more slowly than the corresponding normal alcohols. Also, the purification of the ethers is complicated. The washing-out of the alcohols, as applied to the purification of the C_3–C_5 ethers [2], is not applicable in the present case, since the higher alcohols are practically insoluble in water. The alcohol forms an azeotrope with the vinyl ether, and fractional distillation is of no value. Four or five repetitions of a process consisting in treatment of the vinyl ethers with metallic sodium followed by vacuum distillation from a Favorsky flask and a final fractionation through a column enable pure preparations to be obtained with a yield of 80.4-89.2% (see Table 2). Generally speaking, the yields of the vinyl ethers of higher fatty alcohols are not cited in the foreign literature.

We have established that better results are obtained by carrying out the vinylation of higher fatty alcohols at 140-180° rather than at lower temperatures.

In a review article by Schildknecht and others [3] corrected physical constants are cited for vinyl ethers. However, the boiling points

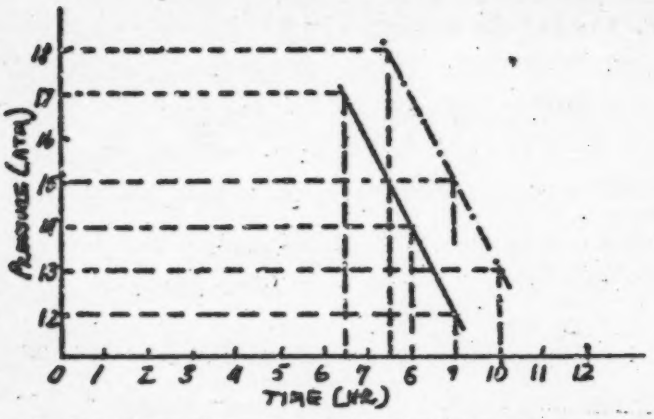

Fig. 2. Dependence of time required for vinylation on complexity of alcohol and on initial pressure: . . . iso-octyl alcohol; —hexyl alcohol. NOTE: 3 mole of alcohol was taken.

of the octyl and decyl ethers are given for reduced pressure (4 and 10 mm), i.e. there is no possibility of following the regular rise in the boiling points of the ethers associated with increasing complexity of the radicals or of deciding the important question of the stability of the ethers to heat. The investigations have shown that the C_8–C_{12} alkyl vinyl ethers can be distilled at ordinary pressure without decomposition. The ethers have lower boiling points than the corresponding alcohols, and they are more mobile. When kept for a long time (6 months or more), the ethers become slightly yellow and partially hydrolyzed. Hydrolysis, of course, is one of the methods for the establishment of the structure and of the purity of alkyl vinyl ethers. Hydrolysis of hexyl vinyl and iso-octyl vinyl ethers (0.15 mole) by means of 5% aqueous sulfuric acid at 70-80° for 3-4 hrs showed that they are completely decomposed into aldehyde and alcohol. The products obtained were characterized by their physical constants.

As will be seen from Table 2, the sp.gr., refractive index, and molecular refraction increase in regular fashion with increase in the molecular weight of the ether in accordance with generally held ideas concerning this homologous series. The experimentally determined molecular weights and the analyses for carbon and hydrogen confirm the purity of the compounds synthesized.

EXPERIMENTAL

We will take as example the vinylation of hexyl alcohol (b.p. 157.8°; n_D^{20} 1.4181). The vinylation was carried out in a 2.6-liter autoclave. The alcohol (306.0 g, 3 mole) and KOH (24 g) were introduced into the autoclave, and acetylene was passed in under a pressure of 18 atm at 26°. The heat was switched on, and the autoclave was set in rotation; the pressure rose to 20-21 atm, but at 140-160° it began to fall. The first two portions of acetylene were fully absorbed, but the next was absorbed only to the extent of 40-70%. When 70-80% of the theoretically calculated amount of acetylene had been absorbed, the rate of absorption fell sharply. In order to intensify the process, the temperature was raised to 180°, thus permitting absorption of acetylene to proceed up to 93-96% of the theoretically possible amount.

When the autoclave had cooled, the residual acetylene was allowed to escape, and the reaction mixture was removed, the autoclave being rinsed out with ether. After standing, the brown reaction mixture separated out into two layers, a liquid upper layer, and a thick, viscous lower layer. The liquid layer was poured off and fractionally distilled; the lower layer was extracted with ether, three or four treatments being required to complete the extraction of organic substances. The extraction is important in order to increase the yield of the vinyl ether. The ether extract was united with the ethereal washings from the autoclave and then distilled.

The crude vinyl ether was treated five times with metallic sodium, and after each treatment it was distilled from a Favorsky flask. Finally, it was distilled through a column of 15-16 theoretical plates having a glass filling. Altogether 342.5 g (89.2%) of a pure preparation was obtained.

Hydrolysis

A mixture consisting of hexyl vinyl ether (19.2 g, 0.15 mole) and 0.1 N H_2SO_4 (15 ml) was placed in a flask fitted with mechanical stirrer and reflux condenser and was heated for 3 hrs at 70-80° on the water-bath. Acetaldehyde was collected in a coil trap connected to the condenser and cooled to −45° by means of solid carbon dioxide in acetone. The yield of acetaldehyde was 6.00 g (91%), and 15 g (98%) of hexyl alcohol was

TABLE 2

Physical Properties of Alkyl Vinyl Ethers

Name and Formula	Yield %	B.p. °C/760 mm	d_4^{20}	n_D^{20}	MR_D found	MR_D calcd.	M found	M calcd.	% C found	% C calcd.	% H found	% H calcd.
Hexyl ether* $H_2C=CHOC_6H_{13}$	89.2	143.5	0.7970	1.4171	40.461	40.480	127.28	128.208	74.85	74.94	12.65	12.58
Heptyl ether $H_2C=CHOC_7H_{15}$	85.1	165.5-166.0	0.8021	1.4220	45.061	45.118	141.95	142.234	75.88	75.99	12.83	12.76
Octyl ether $H_2C=CHOC_8H_{17}$	85.0	186.0-187.0	0.8028	1.4270	49.974	49.756	156.07	156.260	76.92	76.85	13.15	12.90
Iso-octyl ether $H_2C=CHOC_8H_{17}$-iso	84.3	175.2-176.2	0.8019	1.4263	49.959	49.756	155.41	156.260	76.40	76.85	12.90	12.90
Nonyl ether* $H_2C=CHOC_9H_{19}$	80.4	206.1-207.0	0.8089	1.4310	54.421	54.394	170.85	170.286	77.40	77.58	13.11	13.02
Decyl ether* $H_2C=CHOC_{10}H_{21}$	80.5	224.2-225.0	0.8123	1.4347	59.172	59.022	184.04	184.312	78.14	78.19	13.20	13.13
Cyclohexyl ether** $H_2C=CHOC_6H_{11}$-cyclo	86.9	147.4-148.0	0.8883	1.4546	38.514	38.260	126.60	126.192	76.18	76.14	11.07	11.18

* Described for the first time

** Polymerized by heat

obtained; both compounds were characterized by their physical constants (aldehyde, b.p. 20.3°; n_D^{19} 1.3332; alcohol, b.p. 158°; n_D^{20} 1.4181).

SUMMARY

1. A study has been made of the vinylation of the C_6–C_{18} fatty alcohols.

2. The C_8–C_{12} vinyl ethers have been obtained in yields of 80.4-89.2 %.

3. The synthesized vinyl ethers have been characterized by their physical constants.

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DESULFURIZING ACTION OF TROSHKOV KAOLIN

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Although there is a wide literature on the desulfurization of motor fuels, the problem of desulfurization is not yet fully solved. This question, however, is assuming increasing importance now that manufacturing and processing concerns are being supplied with considerable quantities of sulfur-containing petroleums and with tars, containing various amounts of sulfur, derived from coal, shale, and sapropelites. As is well known, sulfur compounds cause corrosion and formation of deposits in engines; they adversely affect the antidetonation characteristics of the fuel, reduce its sensitivity to tetraethyl-lead, and produce a number of other undesirable phenomena. The permitted limit of sulfur in automobile gasolines is 0.15%; the limit for gasolines obtained from sulfur-containing petroleums is 0.4-0.6%. It is necessary, however, to aim at a considerable reduction in these upper limits.

Thus, Semenov [1], investigating the effect of the sulfur content of the gasoline on the functioning of the engine, found that an increase in the sulfur content of the gasoline from 0.05 to 0.6% reduces the power and efficiency of the engine by 25-35% and its service life by at least a quarter. He considers that it is essential to reduce the content of sulfur in gasolines to 0.05-0.07%.

In the present work we have investigated the use of Troshkov kaolin as a desulfurizing agent. As shown in our previous investigations, this kaolin may be used as starting material for the preparation of a good refining catalyst for the treatment of certain fractions of the primary tar from Budagov sapropelites. In order to study its desulfurizing propensity, the Troshkov clay was applied to the treatment of sulfur-containing direct-distillate gasolines and also of desulfurized gasoline to which additions of particular sulfur compounds had been made.

EXPERIMENTAL

The catalyst was prepared from clay that had not been activated with acid. Desulfurization was carried out at atmospheric pressure in the usual flow-type apparatus used for catalysis work. The temperature was measured by means of a thermocouple. Gasoline was passed at a space velocity of 0.3. Before the experiment the furnace was heated to the necessary temperature and air was blown through the catalyst tube in order to dehydrate the catalyst more fully. At the end of the experiment the catalyzate was washed with 10% caustic soda (to remove the hydrogen sulfide formed) and with water. It was then dried with calcium chloride and weighed, and determinations were then made of sulfur ("lamp method"), refractive index, specific gravity, and amount of sulfonatable hydrocarbons.

The original gasoline D, the variety that we used for the most part in our study of the desulfurizing action of Troshkov kaolin, had the following properties: d_4^{20} 0.7390; n_D^{20} 1.4193; sulfur content 0.185%; iodine no. 2.2; sulfonatable hydrocarbons 10% by vol.

Fractional Composition

Commencement of boil		64°	60	% by vol.	141°
10	% by vol.	84°	70	"	153°
20	"	95°	80	"	165°
30	"	107°	90	"	180°
40	"	118°	95	"	192°
50	"	130°	98	"	200°
			2	"	residue + loss

First of all the effect of temperature on the degree of desulfurization of the gasoline was determined. For this purpose 30 ml of catalyst was taken in a catalysis tube of internal diameter 10 mm. In each experiment gasoline was passed in 30 ml portions. Experiments were carried out at 50° intervals from 200 to 500°. The results obtained are given in Table 1.

On the basis of the results obtained we considered the optimum desulfurization temperature to be 400°.

TABLE 1

Effect of Temperature on the Degree of Desulfurization of Gasoline

Gasoline	Temp. of expt. (°C)	n_D^{20}	d_4^{20}	Sulfonatable content, %	Sulfur content, %	Iodine No.
Original gasoline D	—	1.4193	0.7390	10.0	0.185	2.2
Catalyzate	200	1.4160	0.7404	—	0.101	3.6
"	250	1.4165	0.7400	—	0.073	2.9
"	300	1.4170	0.7400	—	0.067	3.0
"	350	1.4168	0.7393	10.0	0.048	2.6
"	400	1.4160	0.7400	11.0	0.031	2.1
"	450	1.4184	0.7406	18.0	0.032	2.0
"	500	1.4190	0.7410	30.0	0.033	2.2

The sulfur content of the gasoline was reduced at this temperature from 0.185 to 0.031%. However, on raising the temperature the degree of desulfurization did not alter (see Table 1). In order to compare thermal and catalytic desulfurization of gasoline, we carried out comparable experiments at 200, 400, and 500° in presence and in absence of catalyst (in the latter case some glass wool was placed in the catalysis tube).

The results in Table 2 show that under these conditions of temperature thermal treatment of gasoline D gives a considerably lower degree of desulfurization than catalytic treatment.

In order to determine the stability of the catalyst and the possibility of its regeneration, prolonged experiments were carried out on the catalytic treatment of gasoline D with Troshkov clay at 400°. The experimental conditions were: 100 ml (74.1 g) of catalyst (length of layer, 62 cm), in a catalysis tube 1.6 cm in diameter; gasoline passed in 100 ml portions; 40 experiments in all. After the passage of 1000 ml of gasoline, the catalyst was regenerated by passing air through it at 500° for 3 hrs 20 min (duration of experiment). The results obtained are given in Table 3.

TABLE 2

Comparative Experiments on the Desulfurization of Gasoline D in presence of Troshkov Clay and of Glass Wool

Gasoline		Temp. of expt. (°C)	n_D^{20}	d_4^{20}	Sulfonatable content, %	Sulfur content %	Iodine No.
Original gasoline D		—	1.4193	0.7390	10.0	0.185	2.2
Condensate obtained in presence of	clay	200	1.4160	0.7404	—	0.101	3.6
	glass wool	200	1.4156	0.7439	—	0.172	3.2
	clay	400	1.4160	0.7400	11.0	0.031	2.1
	glass wool	400	1.4160	0.7438	11.0	0.126	7.7
	clay	500	1.4190	0.7410	30.0	0.033	2.2
	glass wool	500	1.4145	0.7403	13.5	0.097	8.2

Altogether, the catalyst was in work for 133 hrs 20 min, during which time it was regenerated three times. As will be seen from the results in Table 3, its desulfurizing activity did not change. The yield of catalyzate, washed with alkali and dried with calcium chloride, was about 97%.

In each passage of a 100 ml portion of gasoline over the clay, on the average 450 ml of gas was evolved. This gas had the following composition:

Unsaturated substances	10.5%
Hydrogen	55.8%
Oxygen	0.5%
Methane hydrocarbons	32.0%
Nitrogen	1.2%

As will be seen from the results, the sulfur content of catalyzates obtained by passage of the gasoline over fresh catalyst that has not been regenerated (the first 10 experiments) is reduced in comparison with that of the original gasoline by a factor of 5 or 6. The regenerated catalyst, on the other hand, carries the desulfurization much further: in the catalyzates of experiments 15, 16, and 21 the sulfur content is reduced by a factor of 18. The phenomenon of increased activity in aluminum silicate catalysts after regeneration has been noted also in cracking reactions [2]. The combined catalyzate had the following properties: n_D^{20} 1.4185; d_4^{20} 0.7335; sulfonatables 11.0% by vol; 0.018% S; iodine No. 2.1.

TABLE 3

Variation in Catalyst Activity in the Desulfurization of Gasoline D at a Space Velocity of 0.3 at 400°

Expt. No.	n_D^{20}	Sulfur content, %	Expt. No.	n_D^{20}	Sulfur content, %
Original gasoline	1.4193	0.185			
1	1.4160	0.031	Regeneration		
5	1.4155	0.041	21	1.4151	0.011
6	1.4148	0.041	26	1.4155	0.036
10	1.4160	0.037	30	1.4163	0.031
Regeneration			Regeneration		
11	1.4150	0.016	31	1.4150	0.014
15	1.4185	0.010	36	1.4160	0.022
16	1.4156	0.012	40	1.4161	0.030
20	1.4150	0.030			

Fractional Composition

Commencement of boil		60.0°	70	% by vol.	154.0°
10	% by vol.	81.0°	80	"	164.5°
20	"	90.5°	90	"	180.0°
30	"	105.5°	95	"	193.0°
40	"	117.0°	98	"	200.0°
50	"	129.0°	2	"	residue + loss
60	"	141.8°			

TABLE 4

Variation in the Activity of Thermally Activated Catalyst in the Desulfurization of Gasoline

Expt. No.	n_D^{20}	Sulfur content, %
1	1.4185	0.011
6	1.4185	0.013
11	1.4180	0.028
16	1.4170	0.028
21	1.4157	0.035
26	1.4200	0.045
31	1.4220	0.056
36	1.4152	0.059
41	1.4162	0.060
Regeneration		
42	1.4148	0.012

Thus, as a result of the catalytic treatment of the original gasoline D with Troshkov clay at 400°, the sulfur content of the gasoline is reduced by a factor of 10.

The fractional composition of the gasoline obtained is altered somewhat in the "light" direction, as compared with the original gasoline. It is important to note that the process is accompanied by inappreciable losses.

It was of interest to discover whether the great increase in the desulfurizing propensity of the clay caused by regeneration (see Table 3) depends only on thermal action, or whether some other factors are concerned. With this in view, a portion of fresh catalyst (30 ml, 22.9 g; tube diameter 10 mm; length of catalyst layer 160 mm) was heated in a stream of air under the conditions of the regeneration. Gasoline D (30 ml) was then passed over the catalyst at 400° at a space velocity of 0.3. The sulfur content of the gasoline fell to 0.011% (see expt. 1 in Table 4). Without thermal activation of the catalyst, the sulfur content of the gasoline fell to 0.031% (see expt. 1, Table 3). Thus, prior thermal treatment of the clay increases its desulfurizing propensity by a factor of approximately 3.

A further 40 portions of gasoline were passed over the same catalyst before it was regenerated. The results are given in Table 4.

The results given in Table 4 show that the desulfurizing propensity of the catalyst is preserved for a fairly long time, although it does fall in time. After working for 136 hrs 40 min, the catalyst reduces the sulfur content of the gasoline by a factor of 3 (expt. 41, Table 4). The subsequent regeneration of the catalyst leads to the complete recovery of its original activity (expt. 42, Table 4).

We have carried out desulfurization experiments also on two other gasolines: gasolines B and K. The catalyst employed for the desulfurization of gasoline D was used after regeneration, and the conditions of the experiment were as before (400°, space velocity 0.3).

The results of the experiments are shown in Table 5.

Thus, also for these gasolines Troshkov clay is a good desulfurizing catalyst.

TABLE 5

Desulfurization of Gasolines B and K in Presence of Troshkov Clay

Gasoline	n_D^{20}	d_4^{20}	Sulfonatables, % by vol.	Sulfur content, %
Original B	1.4153	0.7484	9.0	0.030
Catalyzate	1.4173	0.7488	9.0	0.007
Original K	1.4178	0.7490	6.0	0.018
Catalyzate	1.4172	0.7551	7.0	0.003

In order to elucidate the effect of the nature of the sulfur-containing compounds on the desulfurization process, we carried out experiments on purified gasoline to which additions of particular sulfur compounds had been made. Gasoline D treated carefully with 3% oleum had the following properties; n_D^{20} 1.4105; d_4^{20} 0.7335; sulfur content 0.003%. To this gasoline, additions were made of propanethiol, thiophene, tetrahydrothiophene, or diisopentyl sulfide so as to give a calculated sulfur content of about 0.2%. Determinations were made of the sulfur contents and refractive indices of these mixtures. The samples obtained were passed in 30 ml portions under the same conditions over the same volume of catalyst; some samples were passed twice in succession. When each new sample had been treated catalytically with the clay, the catalyst was regenerated. The properties of the original mixtures and of the catalyzates are given in Table 6.

TABLE 6

Results of Desulfurization Experiments on Gasoline Containing Particular Sulfur-containing Compounds

Gasoline	n_D^{20}	Sulfur Content %	Notes
Purified gasoline + propanethiol	1.4110	0.180	–
Catalyzate	1.4115	0.007	Odor of hydrogen sulfide in catalyzate
Purified gasoline + thiophene	1.4110	0.203	–
Catalyzate	–	0.138	–
Catalyzate after a second passage	1.4135	0.133	–
Purified gasoline + tetrahydrothiophene	1.4108	0.209	–
Catalyzate	–	0.146	–
Catalyzate after a second passage	1.4140	0.063	–
Purified gasoline + diisopentyl sulfide	1.4112	0.193	–
Catalyzate	–	0.047	Odor of hydrogen sulfide in catalyzate
Catalyzate after a second passage	1.4169	None	Ditto

Thus, a catalyst prepared from Troshkov clay effects almost complete removal from gasoline of sulfur present as mercaptan (96.0%) or as thio-ether (after a double passage). A single passage removes 30% of tetrahydrothiophene sulfur, a double passage removes 70%. The question of the removal of thiophene sulfur is a more complicated one: catalytic treatment of the sample of thiophene-containing gasoline removes only about 34% of the sulfur present, and a second operation has no appreciable effect.

SUMMARY

1. An investigation has been made into the desulfurizing action of Troshkov kaolin on three samples of sulfur-containing gasolines and on mixtures of purified gasoline with propanedithiol, with diisopentyl sulfide, with thiophene, and with tetrahydrothiophene.

2. It has been shown that a catalyst prepared from unactivated Troshkov clay has a high desulfurizing propensity at 400°.

3. It has been found that thermal activation of the clay increases its desulfurizing activity by a factor of about 3.

4. Troshkov clay removes from gasoline not only aliphatic sulfur-containing compounds (mercaptans, thio-ethers), but also cyclic sulfur compounds (tetrahydrothiophene).

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CATALYTIC ALKYLATION OF AMMONIA WITH HALOGEN DERIVATIVES OF ALKANES AND CYCLOALKANES

COMMUNICATION 1

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There is no information in the literature concerning the catalytic alkylation of ammonia in the vapor phase by means of alkyl and cycloalkyl halides. There are, however, a number of investigations on the synthesis of amines by the action of liquid ammonia on certain organic halogen compounds [1]. Work with liquid ammonia is, of course, carried out under pressure in autoclaves, a process that is attended by considerable difficulties. We therefore set ourselves the task of studying the conditions required for the catalytic synthesis of amines of the aliphatic and alicyclic series in a continuous-flow system under ordinary pressure. The vapor-phase method for the catalytic synthesis of amines at atmospheric pressure has great possibilities for the production of these important substances and will be of great value for the further development of the chemistry and technology of amines. As a result of our investigations we have succeeded in finding a suitable catalyst, based on magnesium oxide, which, under suitable conditions, promotes the catalytic synthesis of amines in high yield from alkyl halides.

EXPERIMENTAL

In the selection of catalysts information in the literature on the amination of alcohols and of alkenes was taken into account. However, the most active catalysts for the amination of alcohols (platinized silica gel, etc.) [2] were found to be unsuitable for our purpose; the yield of amine was low when they were used, and at the same time splitting-off of halogen halide with formation of unsaturated hydrocarbons occurred to an appreciable extent. In view of the latter circumstance, it was decided that in further work catalysts employed for the amination of alkenes should be used so that in the moment of formation unsaturated hydrocarbons should be converted into amines.

Teter [3] alkylated ammonia with alkenes in presence of reduced oxides of cobalt and nickel deposited on bentonite that had been treated with acid. As catalysts we tried reduced nickel and cobalt, also their hydroxides and halides on asbestos, charcoal, pumice, kieselguhr, and silica gel. However, they were all found to be unsuitable, for the undesired formation of unsaturated hydrocarbons was found to occur in their presence.

After lengthy investigations we found that amination of the halogen compounds proceeds with a good yield of amines in presence of a catalyst based on magnesium oxide. This catalyst retains its activity for 3.5 hrs, after which it can be regenerated by heating in air to dull red heat or by oxidation with pure air at 350° in the reaction tube itself. Experiments were carried out with 1-chlorobutane, 1-chlorohexane, 1-chloroheptane, 1-chloro-octane, 1-chlorononane, 1-chlorodecane, chlorocyclopentane, chlorocyclohexane, and bromocyclohexane. The properties of the halogen compounds taken for investigation are given in Table 1.

The halogen compounds were introduced by means of an automatic buret into a silica flask, into which gaseous ammonia was passed simultaneously. The flask was heated on an oil bath. The mixture of vapors was directed into a glass tube containing catalyst; the tube was situated in an electric furnace fitted with a thermoregulator. The volume of catalyst was 100 ml in all experiments; the molecular ratio of ammonia and halogen derivative was 2:1; the space velocity was taken to be 0.2 in all experiments. The reaction products were collected in a receiver cooled with ice and salt. The condensates obtained were dried by means of anhydrous sodium sulfate and were analyzed for amine-nitrogen content by Francois' method [4]. The estimation of primary amine was carried out by Van Slyke's method [5]. The content of tertiary amine was estimated by treating the mixture of amines with nitrous acid and titrating the amine subsequently distilled off. The amount of secondary amine was found by difference. The gases formed in the reaction were collected in a graduated gasholder and analyzed by the usual method; hydrogen was estimated by Jager's method [6] by combustion over copper oxide.

TABLE 1

Properties of the Alkyl and Cycloalkyl Halides Used

Substance	B.p. * (°C)	n_D^{20}	d_4^{20}
1-Chlorobutane	78.5	1.4015	0.8840
1-Chlorohexane	135.0	1.4230	0.8779
1-Chloroheptane	159.5	1.4292	0.8745
1-Chloro-octane	184.0	1.4325	0.8869
1-Chlorononane	190.0	1.4402	0.8806
1-Chlorodecane	223.0	1.4381	0.8702
Chlorocyclopentane	114.0	1.4497	1.0025
Chlorocyclohexane	142.0	1.4627	0.9987
Bromocyclohexane	163.0	1.4958	1.3241

Of all the catalysts tried, one based on magnesium oxide gave the best results for the alkylation of ammonia by means of the halogen compounds taken for investigation (see Tables 2 and 3). Low yields were obtained in presence of the other catalysts tried.

SUMMARY

1. The catalytic alkylation of ammonia in the gas phase at ordinary pressure has been carried out with good yields by means of halogen derivatives of alkanes and cycloalkanes.

2. Of various catalytic agents tried, the most effective was found to be a catalyst prepared from magnesium oxide.

3. The amine contents of the catalyzates obtained in presence of this catalyst at 310° in the reactions between ammonia and chloroalkanes (1-chlorobutane, 1-chlorohexane, 1-chloroheptane, 1-chloro-octane, 1-chlorononane, and 1-chlorodecane) (space velocity 0.2) were 60.0, 60.5, 61.0, 63.0, 77.0, and 78.6% respectively.

TABLE 2

Synthesis of Aliphatic Amines at 310° in Presence of a Catalyst Prepared from Magnesium Oxide

Chloroalkane	Yield of condensate, % of orig. chloroalkane	Amine nitrogen in catalyzate, %	Yield of amine (%)		
			primary	secondary	tertiary
1-Chlorobutane	80.5	11.4	39.2	18.1	2.7
1-Chlorohexane	82.1	12.0	45.0	13.0	2.5
1-Chloroheptane	84.1	11.8	50.5	9.0	1.5
1-Chloro-octane	83.2	10.5	58.0	4.2	0.8
1-Chlorononane	83.5	9.7	69.0	8.0	–
1-Chlorodecane	84.4	8.7	70.6	8.0	–

NOTE. Duration of each experiment: 1 hr.

TABLE 3

Synthesis of Alicyclic Amines at 340° in presence of a Catalyst prepared from Magnesium Oxide

Halogen derivative	Yield of condensate, % of orig. halogen deriv.	Amine nitrogen in catalyzate, %
Chlorocyclopentane	98.1	11.5
Chlorocyclohexane	97.7	10.2
Bromocyclohexane	97.5	9.7

NOTE. Duration of each experiment: 1 hr.

4. The effect has been studied of the length of the carbon chain in alkyl halides on the yield of amines, and it has been shown that with increase of chain length from C_4 to C_{10} the amine content of the catalyzate rises from 60.0 to 78.6%.

5. In presence of the same catalyst at 340° and under otherwise identical conditions, chlorocyclopentane, chlorocyclohexane, and bromocyclohexane yield catalyzates containing 11.5, 10.2 and 9.7% of amine nitrogen respectively.

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THE PREPARATION OF STYRENE BY CATALYTIC DEHYDROGENATION OF THE ETHYLCYCLOHEXANE FRACTION OF MAIKOP GASOLINE

N. I. Shuikin and I. I. Levitsky

Catalytic dehydrogenation of ethylbenzene is the most widely used method for the preparation of styrene and is the method that has received the greatest amount of study [1,2]. The reaction occurs at 600-650° in presence of difficultly reducible metal oxides as catalysts. The yield of styrene is greatly increased by diluting the ethylbenzene vapor by, e.g., carbon dioxide, steam, or nitrogen. One of the first investigations in this field was that of Zelinsky and coworkers [3]; in this a study was made of a number of catalysts for the dehydrogenation of ethylbenzene and of the way in which temperature, nature of diluent, degree of dilution, and other factors affected the course of the reaction. These investigations showed that oxide catalysts based on copper-chromium or on vanadium-aluminum are of high activity and are readily regenerated.

The reaction, discovered by Zelinsky, by which cyclohexane and its homologs are dehydrogenated over palladium or platinum black has served as a basis for the development of a new method for the study of the chemical nature of gasolines [4,5,6,7]. This reaction, in which the six-membered cycloalkanes are converted smoothly into the corresponding aromatic hydrocarbons at 300°, is the basis of a well-tried method for the exhaustive catalytic aromatization of gasolines [8]. The oxide catalysts (chromium oxide, vanadium oxide, etc.), also are able to initiate dehydrogenation of cyclohexane hydrocarbons, but the reaction occurs at a higher temperature (450-475°) and is complicated by side-reactions [9].

We considered that it would be interesting to investigate the possibility of extending the method for the dehydrogenation of cycloalkanes to the catalytic synthesis of styrene from the ethylcyclohexane of petroleum. Two methods for this synthesis can be envisaged: a) catalytic aromatization of the ethylcyclohexane fraction of gasoline over platinized charcoal and subsequent dehydrogenation of the ethylbenzene obtained (in admixture with xylenes, alkanes, and five-membered cycloalkanes) over an oxide catalyst, and b) separation of ethylbenzene and of xylenes from the aromatized (300°) ethylcyclohexane fraction and subsequent catalytic dehydrogenation of ethylbenzene. Also a third variant of the synthesis may be pointed out — direct dehydrogenation of the ethylcyclohexane fraction over oxide catalysts to styrene, i.e. simultaneous dehydrogenation of the cyclohexane ring and of the ethyl substituent.

Investigations in this direction have been carried out by one of us in conjunction with Usov and Marukyan [10]; we studied the dehydrogenation of the ethylcyclohexane fraction (127-134°) of Maikop gasoline over a copper-chromium oxide catalyst at 625° in a stream of carbon dioxide. The catalyzates obtained contained 21.0-31.3% of styrene. Dehydrogenation under similar conditions of a previously aromatized (300°) ethylcyclohexane fraction of the same gasoline yielded catalyzates containing 20-25% of styrene. Thus, two variants of the synthesis of styrene from the ethylcyclohexane of petroleum have been explored. The present work constitutes a continuation and development of the above investigation.

The dehydrogenation of the ethylcyclohexane fraction of Maikop gasoline and of the product of its smooth catalytic aromatization at 300° was carried out by us at 575° over a catalyst based on the oxides of vanadium and aluminum. By changing the reaction conditions with respect to those used in the previous work, we endeavored to restrict, as far as possible, destruction of the hydrocarbons. Separation of the ethylcyclohexane fraction of the gasoline was carried out by the aid of a considerably more efficient column. The determination of the combined content of ethylcyclohexane and natural ethylbenzene was carried out by Ullmann's oxidation method. The results of this determination were lower than those obtained in the previous work [10] by the Raman-spectrum method. This divergence is probably due to a difference in chemical composition between the two different samples of Maikop gasoline taken for investigation and also, possibly, to the use of an insufficiently pure ethylbenzene standard.

In the present work we investigated also the third variant of the catalytic synthesis of styrene from the ethylcyclohexane fraction: separation of an ethylbenzene-xylene concentrate followed by its dehydrogenation.

EXPERIMENTAL

Separation of the Ethylcyclohexane Fraction, B.p. 127-134°

For the investigation we took the Maikop straight-distillate gasoline, containing 8% of aromatic hydrocarbons and characterized by the following constants: boiling limits 41-165°; d_4^{20} 0.7630; n_D^{20} 1.4125. The head fraction (up to 103°) of the gasoline was separated by the use of a laboratory column of 7-8 theoretical plates. The remainder was carefully fractionated through a column of 19 theoretical plates, and the fraction of b.p. 127-134° was separated. This fraction had d_4^{20} 0.7792; n_D^{20} 1.4341 and contained 26% aromatic hydrocarbons.

Aromatization of the Ethylcyclohexane Fraction

The fraction of b.p. 127-134° was aromatized smoothly by passage over platinized charcoal at a space velocity of 0.3* at 300°. The high activity of the catalyst with respect to cyclohexane was characterized by the refractive index of the catalyzate n_D^{20} 1.4945. The catalyzate obtained from the ethylcyclohexane fraction contained 47% of aromatic hydrocarbons and had n_D^{20} 1.4479 and d_4^{20} 0.7965. A second passage over the catalyst changed the refractive index only slightly to n_D^{20} 1.4485. Thus, the aromatization of the ethylcyclohexane fraction was almost complete after the first operation.

Determination of the Content of Ethylbenzene in the Catalyzate

The estimation of ethylbenzene was carried out by treatment of the catalyzate with a 5% alkaline solution of permanganate (which oxidizes the ethylbenzene and xylenes contained in the catalyzate) according to the method described by Moldavsky and coworkers [11], with the modifications introduced by Maslyansky and Berlin [12]. It was found that the distribution of aromatic hydrocarbons in the catalyzate was as follows: 35.5% of ethylbenzene, 28.4% of o-xylene, and 36.1% of m- and p-xylenes.

The ethylbenzene in the catalyzate consisted of natural ethylbenzene and of the ethylbenzene formed by dehydrogenation of ethylcyclohexane. As noted above, the catalyzate contained 47% of aromatic hydrocarbons. Hence, the combined content of natural ethylbenzene and ethylcyclohexane in the original fraction (and so of ethylbenzene in the catalyzate) was (47 x 35.5)/100 = 16.7%. In order to increase the concentration of ethylcyclohexane in the fraction, a more efficient column and a narrower distillation-temperature range would probably be required; however, separation of a fraction within a range of less than 6-7° leads to incomplete extraction of ethylcyclohexane from the gasoline.

The lowness of the concentration of ethylcyclohexane in the original fraction and also, therefore, of ethylbenzene in the aromatization product from this fraction decided the main course of further work: separation and investigation of an ethylbenzene-xylene concentrate. The second of the dehydrogenation variants referred to above was therefore taken as the basis of the main line of investigation.

Separation of the Ethylbenzene-Xylene Concentrate

In order to separate ethylbenzene and xylenes from the product of the smooth catalytic aromatization of the 127-134° fraction, we made use of azeotropic distillation with methanol [13]. There are indications in the literature [14] that this method is unsatisfactory when the boiling points of the azeotropic component (methanol) and of the hydrocarbons that are removed with it differ by more than 50°. This method was therefore checked on an artificial mixture of ethylbenzene and the dearomatized gasoline fraction (b.p. 134-138° after treatment with 3% oleum). It was established in this way that methanol is quite suitable for the separation of ethylbenzene from the corresponding gasoline fraction.

In order that the separation of ethylbenzene from the aromatization product from the 127-134° fraction should be as complete as possible, we carried out the fractionation with a large excess of methanol. The operation was carried out in two stages. Methanol was added to the aromatization product so that the ratio of non-aromatics to methanol became 1:2 or 1:3. The mixture obtained was distilled through a column of 19 theoretical plates, azeotrope being separated up to 64-65°. The residue contained 70-80% of aromatic hydrocarbons. Further methanol was added to the residue to give a non-aromatic/methanol ratio of 1:7, and a second fractionation yielded a residue containing aromatic hydrocarbons and methanol and practically no alkanes or cycloalkanes. The aromatic hydrocarbons were readily freed from methanol by washing with water.

* The space velocity, both here and later, is expressed in liters of substance passing in one hour over one liter of catalyst.

As an example, we will give the results of such a distillation: Aromatization product (351 g) and methanol (328 g) were distilled through a column of 19 theoretical plates, and 435 g of azeotropic mixture was collected. Methanol (600 g) was then added to the residue, and after a second fractionation 163 g of an ethylbenzene-xylene concentrate. After being freed from methanol and dried over calcium chloride, it came over when distilled over sodium in the range 136-146°, had n_D^{20} 1.4970, d_4^{20} 0.8712, and consisted entirely of aromatic hydrocarbons.

It was established above that the aromatic hydrocarbons in the catalyzate from the 127-134° fraction consisted of 35.5% ethylbenzene and 64.5% xylenes. The concentrate that we obtained, to which we shall refer in future as the ethylbenzene-xylene concentrate, had the same composition.

Procedure Used for the Dehydrogenation of the Ethylbenzene-Xylene Concentrate, of the Ethylcyclohexane Fraction, and of the Product of the Catalytic Aromatization of the Latter at 300°

Dehydrogenation was carried out over a catalyst based on vanadium and aluminum oxides. The catalyst was contained in a silica tube, 20 mm in diameter. The tube was placed in an electric furnace, which was provided with a thermoregulator and a mercury relay. The temperature was measured by means of a thermocouple, contained in a silica jacket inserted in the layer of catalyst and connected to a potentiometer. Temperature variations were not greater than ±1°. At the entrance to the reaction tube there was a three-way junction connecting the thermocouple, the automatic buret for delivery of the material to be dehydrogenated, and a Kipp's carbon dioxide generator. The rate of delivery of carbon dioxide was regulated by the aid of a flow-meter. At its exit the reaction tube was connected to a receiver, which was well cooled in ice. The content of styrene in the dehydration catalyzate was determined by titration according to Rosenmund's method [15]. In all experiments the material to be dehydrogenated was diluted with carbon dioxide, the volume ratio being kept constant (5.6 liter of CO_2 to 15 ml of liquid material).

Dehydrogenation of the Ethylbenzene-Xylene Concentrate

The principal results obtained in the dehydrogenation of the ethylbenzene-xylene concentrate are given in Table 1. For comparison, results are given of experiments on pure ethylbenzene carried out under similar conditions. The last column of the table contains values for the degree of conversion of ethylbenzene into styrene. These values are calculated from the ratio (a·100)/b, where a is the styrene content of the dehydrogenation catalyzate, and b is the ethylbenzene content of the material to be dehydrogenated.

The high degree of conversion of the ethylbenzene present in the ethylbenzene-xylene concentrate in comparison with that of pure ethylbenzene is noteworthy. An increase in the degree of dehydrogenation of ethylbenzene occurring when it is diluted with xylenes has been noted by other investigators. Marukyan [16] studied the dehydrogenation of ethylbenzene in admixture with xylenes at 625° over a catalyst based on copper and chromium oxides and established that reduction of the concentration of ethylbenzene in the initial mixture of 34% results in its being completely dehydrogenated.

Determination by the Polymerization Method of the Styrene Content of the Catalyzates Obtained by Dehydrogenation of the Ethylbenzene-Xylene Condensate

The combined catalyzates from a number of experiments on the dehydrogenation of the ethylbenzene-xylene concentrate was found by Rosenmund's titration method to contain 22.8% of styrene. It was considered interesting to check this result by another method. For this purpose, the catalyzate (81 g) and benzoyl peroxide (0.8 g) were sealed in a tube, which was heated at 150° for 50 hrs. The catalyzate that had been treated in this way was distilled from a Claisen flask under 150 mm pressure. The greater part of it distilled in the range 85-90° and had n_D^{20} 1.4985. The residue was then placed under vacuum, warmed gently until effervescence ceased, and allowed to cool. 19.4 g of solid yellow polymer was obtained, i.e. 22.9% of the weight of original catalyzate (after making a correction for benzoyl peroxide). Hence, the value of the styrene content of the dehydrogenation catalyzate determined by titration is almost identical with that obtained by the polymerization method.

Dehydrogenation of the 127-134° Fraction and of the Product of its Smooth Aromatization

The original fraction of b.p. 127-134° contained only 16.7% of ethylcyclohexane. An investigation of the direct dehydrogenation of ethylcyclohexane to styrene at such low concentrations could not give satisfactory results.

TABLE 1

Dehydrogenation of the Ethylbenzene-Xylene Concentrate at a Space Velocity of 0.3

Temp. of expt. °C	Material to be dehydrogenated	Amt. of material taken (g)	Catalyzate obtained (g)	Yield of catalyzate % on material taken	Styrene content of catalyzate %	Degree of conversion of ethylbenzene %
575	Ethylbenzene-xylene concentrate	13.1	10.5	80	19.3	68
575	Pure ethylbenzene	13.1	11.5	88	43.1	43
600	Ethylbenzene-xylene concentrate	14.8	10.8	73	20.8	74
600	Ditto	14.8	10.7	72	20.8	74
600	Pure ethylbenzene	14.9	11.7	78	50.9	51

Nevertheless, comparison of the results of the dehydrogenation of the original fraction with those for the product of its smooth aromatization permitted an approximate appraisal of the effectiveness of prior aromatization of the fraction. Such a comparison made it possible to find out whether the first variant for the dehydrogenation of the ethylcyclohexane fraction referred to above has any advantage.

It may be expected that dehydrogenation of ethylcyclohexane to styrene proceeds in two stages:

$$C_6H_{11}C_2H_5 \longrightarrow C_6H_5C_2H_5 + 3H_2 \longrightarrow C_6H_5CH{=}CH_2 + 4H_2.$$

The first stage of this reaction has already been realized in the smooth aromatization of the ethylcyclohexane fraction; simultaneously, dimethylcyclohexanes present in the fraction were dehydrogenated also, giving xylenes. The comparison referred to above showed, therefore, whether the performance of this reaction in two distinct stages (ethylcyclohexane being present in the fraction at low concentration) could lead to better results than direct dehydrogenation of ethylcyclohexane to styrene. The results of the dehydrogenation of the 127-134° fraction and of its aromatization product are given in Table 2. A measure of the activity of the catalyst is obtained from the results of experiments on pure ethylbenzene, which were produced under similar conditions.

The results of the experiments showed that prior aromatization of the original 127-134° fraction had no appreciable effect on the results of the subsequent dehydrogenation of this fraction. The styrene content of the catalyzates produced by dehydrogenation of the original fraction was practically identical to that of the catalyzates produced by dehydrogenation of the product of the smooth aromatization of this fraction. Hence, the first variant of the dehydrogenation of the ethylcyclohexane fraction (for low concentrations of ethylcyclohexane in the fraction) has no advantage over the third variant (see above), and performance of the reaction in two distinct stages gives results that do not differ under the conditions investigated from results obtained by the direct dehydrogenation of ethylcyclohexane to styrene. It should be noted that the results of these experiments are in agreement with the results of one of us, working with Usov and Marukyan [10].

The results that we have obtained have prompted us to investigate the dehydrogenation of pure ethylcyclohexane to styrene. The results of this work will be published later.

SUMMARY

1. A study has been made of the conditions required for the catalytic dehydrogenation with formation of styrene of the ethylcyclohexane fraction (127-134°) of Maikop straight-distillate gasoline in contact with a catalyst based on the oxides of vanadium and aluminum.

2. Results have been obtained for dehydrogenation to styrene under different conditions of the fraction mentioned, of the catalyzate obtained by the smooth dehydrogenation of the six-membered cycloalkanes (ethyl- and dimethyl-cyclohexanes) contained in the fraction in presence of platinized charcoal at 300°, and also of an ethylbenzene-xylene concentrate obtained from this catalyzate.

3. It has been shown that as a result of dehydrogenation of the ethylcyclohexane fraction, and also of the product of its catalytic aromatization at 300°, 11-14% of styrene is obtained. When the catalytic dehydrogenation is carried out on the ethylbenzene-xylene concentrate, the yields of styrene rise to 22-23%.

TABLE 2

Dehydrogenation of the 127-134° Fraction and of the Product of its Smooth Aromatization

Expt. No.	Temp. of expt. (°C)	Material to be dehydrogenated	Space velocity	Amt. of material taken, g	Catalyzate obtained (g)	Yield of catalyzate % on material taken	Styrene content of catalyzate (%)
12	547	Pure ethylbenzene	0.31	13.1	11.5	88	32.5
15	547	Product of aromatization of fraction	0.30	11.8	10.1	86	12.4
17	547	127-134° fraction	0.30	11.8	9.7	82	10.9
20	547	Ditto	0.14	11.7	8.6	73	13.5
24	575	Pure ethylbenzene	0.30	13.1	11.5	88	43.1
16	575	Product of aromatization of fraction	0.30	11.8	8.4	71	13.8
18	575	127-134° fraction	0.30	11.7	7.6	65	11.3
19	575	Ditto	0.14	15.6	8.8	56	12.2

4. It has been shown that prior aromatization of the original fraction has no appreciable effect on the results of its high-temperature dehydrogenation.

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HEXADECYL ESTERS OF CERTAIN INORGANIC ACIDS

B. A. Arbuzov and V. S. Vinogradova

In the course of work on the structures of esters of inorganic acids, which we studied by the aid of parachor [1] and viscosity measurements, we found it necessary to synthesize esters containing long hydrocarbon radicals. We have recently synthesized a number of esters, including the hexadecyl esters of phosphorous, silicic, and boric acids. We found that these esters, in spite of their high molecular weights, could be distilled in a high vacuum.

We prepared trihexadecyl phosphite by transesterification of triethyl phosphite with 1-hexadecanol in presence of a small amount of phosphoric acid. It is a colorless liquid, non-wetting to glass; it has b.p. 288-290°/4 mm, and it crystallizes at room temperature to a white mass, m.p. 46-47°. After recrystallization from hexane under cooling, trihexadecyl phosphite has m.p. 51°.

Davey [2] has recently prepared trihexadecyl phosphite by the action of phosphorus trichloride in hexadecanol in presence of pyridine. Davey gives the m.p. as 67° and does not indicate the b.p. We have subjected the substance to repeated recrystallization, but have been unable to obtain a melting point of 67°. Tetrahexadecyl orthosilicate was prepared by Helferich and Hausen [3] as a solid of m.p. 46.5-49.5°. Attempts to distil it under reduced pressure failed.

We have prepared tetrahexadecyl orthosilicate by the transesterification of the tetraethyl ester with hexadecanol. The tetrahexadecyl ester distils in a high vacuum without any signs of decomposition; it is a colorless transparent liquid, rapidly crystallizing on cooling: b.p. 353-355°/0.0117 mm or 363-366°/0.2 mm; m.p. 44.5-45°. It should be mentioned that tetrahexadecyl orthosilicate contains 64 carbon atoms and has a molecular weight of about 1000 (995.0).

Trihexadecyl borate was obtained by the esterification of boric acid with hexadecanol. It is a colorless liquid, non-wetting to glass, b.p. 328-329°/< 0.5 mm; rapidly crystallizes at room temperature, m.p. 43-44°.

EXPERIMENTAL

Distillation of the esters was carried out from a Claisen-type flask containing glass wool and having a long exit tube fused on in a low position; the receivers were fused on to this tube, and the selection of fractions was made by rotating the whole apparatus. When distillation was complete, the receivers were fused off.

Trihexadecyl Phosphite. Triethyl phosphite (3.5 g) and 1-hexadecanol (14 g) were introduced into the distillation flask, and sirupy phosphoric acid (2 drops) was added. On heating, alcohol (2.2 g) was driven off. In the course of distillation a small amount of hexadecanol passed over, and this was followed by a colorless liquid, b.p. 288-290°/4 mm. Redistillation yielded hexadecanol and a small amount of the phosphite, m.p. 46-47°. Recrystallization from hexane, with cooling to 0°, yielded a product of m.p. 51°.

Found %: P 4.44

$C_{48}H_{99}O_3P$. Calculated %: P 4.10

Tetrahexadecyl Orthosilicate. 30 g of hexadecanol and 5.3 g of the ethyl ester were taken. No ethanol came over on heating. Phosphoric acid (2 drops) was added. Alcohol (4.2 g) came over. The final temperature of the bath was 220°. When the mixture was distilled, a small amount of hexadecanol was driven off, and then, at 362-365°/0.1 mm, a colorless transparent liquid came over; it rapidly crystallized on cooling. After repeated distillation: b.p. 353-355°/0.0117 mm, 363-366°/0.2 mm; m.p. 44.5-45°.

Trihexadecyl Borate. 1-Hexadecanol (10 g) and boric acid (0.85 g) were placed in a flask and heated. Water came off (bath temperature up to 200°) and was removed towards the end of the reaction under suction from a water pump. In the course of distillation under high vacuum, first a little hexadecanol came over, and there followed a colorless liquid, b.p. 328-331°/< 0.5 mm which did not wet glass; it crystallized in the receiver to give a white waxlike mass. After repeated distillation; b.p. 328-329°/< 0.5 mm, m.p. 43-44°; yield 80%.

Found %: B 1.38

$C_{48}H_{99}O_3$ Calculated %: B 1.46

SUMMARY

Trihexadecyl phosphite and tetrahexadecylorthosilicate have been prepared by transesterification of the ethyl esters of the corresponding acids by means of 1-hexadecanol. Trihexadecyl borate has been prepared by the action of 1-hexadecanol on boric acid. All the esters obtained may be distilled in a high vacuum without decomposition.

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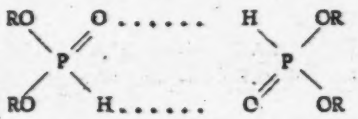
VISCOSITY AND STRUCTURE OF DIALKYLPHOSPHOROUS ACIDS**

B. A. Arbuzov and V. S. Vinogradova

On the basis of studies of Raman spectra, A. E. Arbuzov, Batuev, and Vinogradova [1] concluded that the lower dialkylphosphorous acids are associated, forming dimers by the aid of hydrogen bonds



We came to similar conclusions for the lower members of the series from a study of their parachors [2] and from direct molecular weight determinations in benzene solution [3]. Dimethylphosphorous acid is found in the monomeric condition only in very dilute solution.

TABLE 1

Name of acid	Solvent	Concentration %	η_{sp}^{20} (1.4%)·10^{-3}	η_{sp} (1.4%)·10^{-4} calculated		Z_η·10^{-4} found	Z_η·10^{-4} calculated	
				monomer	dimer		monomer	dimer
Dibutylphosphorous	CCl_4	2.82	11.3	16.5	21.0	8.1	11.9	15.1
		3.83	13.6			9.7		
		5.35	12.8			9.1		
Dihexylphosphorous	CCl_4	2.68	24.0	22.5	27.0	17.2	16.2	19.4
		3.70	22.4			16.1		
		4.01	20.0			14.2		
Dicyclohexylphosphorous*	C_6H_6	3.66	16.3	19.5	23.4	11.6	14.0	16.7
		5.51	18.0			12.8		
Dioctylphosphorous	CCl_4	2.62	22.5	28.5	33.0	16.1	20.5	23.8
		3.15	23.9			17.2		
		5.07	24.1			17.2		
Dinonylphosphorous	CCl_4	2.68	31.5	31.5	36.0	22.5	22.7	25.9
		3.48	26.7			19.0		
Didecylphosphorous	CCl_4	2.91	30.2	34.5	39.0	21.6	25.0	28.1
		3.18	33.1			23.7		
Dihexadecylphosphorous	CCl_4	2.70	55.2	52.5	58.5	39.4	37.8	42.1
		2.44	56.5			40.3		

The higher members of the dialkylphosphorous acid series (dihexyl-, diheptyl-, dioctyl-phosphorous acids) are monomeric both in solution, and in the liquid state. Kosalapoff [4] has found by molecular weight determinations in dilute benzene and naphthalene solutions that diethyl- and dibutyl-phosphorous acids are monomeric. The infrared spectra of the lower dialkylphosphorous acids point to their association [5]. Staudinger [6] showed that measurements of the viscosity of the higher fatty acids in dilute solution indicate that they are associated into dimers.

In the present communication we give our results on the measurement of the viscosities of solutions of dialkylphosphorous acids containing fairly long hydrocarbon radicals (Table 1).

* For calculation of the theoretical value of the viscosity, a six-membered ring is taken as six members.

** The original terminology is retained, dialkylphosphorous acid being a non-committal term for what may be a dialkyl phosphonate, a dialkyl hydrogen phosphite, or a tautomeric mixture of these. - Publisher.

TABLE 2

Name of acid	Solvent	Concentration %	$\eta^{20}_{equiv} \cdot 10^{-3}$ of monomer		$\eta^{20}_{equiv} \cdot 10^{-3}$ of dimer	
			found	calculated	found	calculated
			η (1.76%)		η(2.06%)	
Dibutylphosphorous	CCl_4	2.82	14.3	21.0	16.6	31.2
		3.83	17.2		20.0	
		5.35	16.1		18.8	
			η(1.67%)		η(2.78%)	
Dihexylphosphorous	CCl_4	2.68	28.7	27.0	47.8	54.1
		3.70	26.8		44.7	
		4.10	23.8		39.6	
			η(1.64%)		η(2.73%)	
Dicyclohexylphosphorous	C_6H_6	3.06	19.1	22.9	31.8	45.8
		5.51	21.1		35.1	
			η(1.61%)		η(2.21%)	
Dioctylphosphorous	CCl_4	2.62	26.0	33.1	35.1	66.2
		3.15	27.6		38.0	
		5.07	27.7		28.1	
			η(1.59%)		η(2.78%)	
Dinonylphosphorous	CCl_4	2.68	35.8	36.1	62.7	72.2
		3.48	30.3		53.1	
			η(1.57%)		η(2.79%)	
Didecylphosphorous	CCl_4	2.91	34.1	39.1	60.4	78.3
		3.18	37.3		66.0	
			η(1.51%)		η(2.72%)	
Dihexadecylphosphorous	CCl_4	2.70	59.6	57.3	107.4	114.6
		2.44	60.9		109.8	

As the results in Table 1 show, the values of η_{sp} (1.4%) and Z_η, calculated for the monomeric and for the dimeric forms of the dialkylphosphorous acid, do not differ greatly, but the experimentally found values correspond more closely to the monomeric forms.

A clearer picture is obtained for the values of η_{equiv}, which takes into account not only the length of the longest chain in the molecule, but also the weight of the whole molecule in its relation to the members of the longest chain [7]. The results obtained are given in Table 2.

The results in Table 2 show that, according to viscosity measurements, the dialkylphosphorous acids occur in the monomeric form.

EXPERIMENTAL

The dialkyphosphorous acids were prepared by the action of phosphorous trichloride on the corresponding alcohols, or by the transesterification of diethylphosphorous acid. The following acids were prepared by the action of phosphorous trichloride on the corresponding alcohols:

1. Dibutylphosphorous acid: b.p. 115° at 10 mm; n_D^{20} 1.4240; d_4^{20} 0.9888 [8].

2. Dihexylphosphorous acid: b.p. 145-146° at 2 mm; n_D^{20} 1.4335; d_4^{20} 0.9486 [8].

3. Dioctylphosphorous acid: b.p. 185-187° at 2 mm; n_D^{20} 1.4422; d_4^{20} 0.9286 [8].

4. Dicyclohexylphosphorous acid: b.p. 155-155.2° at 2 mm; n_D^{20} 1.4778; d_0^{20} 1.0815 [9].

Dihexyl- and dioctyl-phosphorous acids were obtained also by the transesterification reaction. Dinonyl-, didecyl-, dihexadecyl-, bis(β-phenylethyl)-, (ethyl)hexyl-, and (ethyl)octyl-phosphorous acids were obtained for the first time.

Viscosity results for (ethyl)-hexylphosphorous acid are not given, for the chain is not sufficiently long for viscosimetric determinations. The viscosities of (ethyl)octyl- and bis(β-phenylethyl)-phospherous acids were not determined.

Transesterification of diethylphosphorous acid by the higher alcohols was carried out in presence of 1-2 drops of concentrated phosphoric acid. When ethanol had ceased to come over, the residue was vacuum-distilled. In the distillation there were obtained appreciable intermediate fractions that gave, on being repeatedly distilled, an appreciable amount of dialkylphosphorous acids containing higher radicals. It is very probable that in the course of the fractionations there is a redistribution of the radicals of the mixed esters of phosphorous acid that have been formed.

Transesterification of Diethylphosphorous Acid by Hexyl Alcohol

The amounts taken were: diethylphosphorous acid 7 g, hexyl alcohol 14 g (theoretical: 10 g). Ethanol began to come over at a bath temperature of 140-150°; 5.5 ml came over. 5.5 g of hexyl alcohol and intermediate fractions came over and 10 g of the fraction b.p. 142-150°/4 mm. A second distillation gave dihexylphosphorous acid (6 g): b.p. 138.5-139° at 2 mm; n_D^{20} 1.4332.

Transesterification of Diethylphosphorous Acid by Octyl Alcohol

Carried out by a similar method. B.p. 191-192° at 4.5 mm; d_0^{20} 0.9263; n_D^{20} 1.4410.

Transesterification by Nonyl Alcohol

The amounts taken were: diethylphosphorous acid 7 g, nonyl alcohol 15 g. Alcohol began to come over at a bath temperature of 150°. 4.5 ml of alcohol was driven off. On fractionation there was obtained 9 g of a fraction b.p. 199-206° at 4 mm. On redistillation there was obtained dinonylphosphorous acid, b.p. 211-212° at 5 mm; 174.5-175.5° at 0.04 mm; n_D^{20} 1.4458; d_0^{20} 0.9212.

Found %: P 9.33; 9.58
$C_{18}H_{39}O_3P$. Calculated %: P 9.26

Transesterification by Decyl Alcohol

The amounts taken were: diethylphosphorous acid 5 g, decyl alcohol 13 g. 3.5 ml of ethanol was driven off. Fractionation yielded 8 g of fraction, b.p. 187-194° at 0.03 mm. Refractionation gave didecylphosphorous acid, b.p. 190-191° at 0.04 mm; n_D^{19} 1.4502; d_0^{23} 0.9157.

Found %: P 8.63; 8.55
$C_{20}H_{43}O_3P$. Calculated %: P 8.54

Transesterification by β-Phenylethanol

The amounts taken were: diethylphosphorous acid 10 g, β-phenylethanol 23 g (theoretical: 17.5 g). 8 ml of alcohol was driven off. On distillation in high vacuum, the following fractions were obtained:

Fraction 1, b.p. to 173° at 0.05 mm
Fraction 2, b.p. 173-209° at 0.05-0.1 mm — 9.5 g.

Decomposition set in. A large residue remained in the flask as a transparent viscous mass. Fraction 2 has a beautiful violet fluorescence. On redistillation it gave a fraction, b.p. 183.5-185.5° at 0.05 mm; n_D^{21} 1.5465; d_0^{20} 1.1333. The substance has a beautiful violet fluorescence.

Found %: P 10.25
$C_{16}H_{29}O_3P$. Calculated %: P 10.69

Transesterification by Hexadecyl Alcohol

The amounts taken were: diethylphosphorous acid 5 g, hexadecyl alcohol 18 g. Alcohol began to come over at a bath temperature of 170°. Towards the end the bath temperature was raised to 220°. On distillation

the following fractions were obtained:

Fraction 1, b.p. 115-130° at 0.07 mm – 11 g
Fraction 2, b.p. 130-230° at 0.1 mm

At this point decomposition set in, and low-boiling fractions came over. On refractionation of fraction 2, decomposition again set in with formation of readily volatile products. Fractionation of fractions 1 and 2 over sodium gave a product that corresponded, according to its constants, to 1-hexadecene: b.p. 126-129° at 3 mm; n_D^{17} 1.4462; d_4^{20} 0.7870.

Duplicate experiment. The amounts taken were: diethylphosphorous acid 4.5 g and hexadecyl alcohol 15 g. Alcohol began to come over at 150°, and 2 ml was collected. Volatile products were driven off in a high vacuum in an apparatus having fused-on receivers. When the temperature on the thermometer was 230° and the pressure was 0.015 mm, boiling commenced, but slight decomposition occurred at the same time and distillation was stopped. A transparent, colorless liquid remained in the flask; on standing, it crystallized (11 g, m.p. 44-45°). M.p. after recrystallization from hexane: 51-52°. M.p. in admixture with hexadecyl alcohol: 51-52°. However, analysis showed that the substance was dihexadecylphosphorous acid.

Found %: P 5.84
$C_{32}H_{67}O_3P$. Calculated %: P 5.84

Preparation of (Ethyl)-hexylphosphorous Acid

The amounts taken were: diethylphosphorous acid 14 g, hexyl alcohol 10 g. Alcohol began to come over at a bath temperature of 170°; 5.5 ml of alcohol was collected. Fractionation gave the following fractions:

Fraction 1, b.p. to 95° at 2 mm
Fraction 2, b.p. 96-106° at 2 mm
Fraction 3, b.p. 106-149° at 2 mm

After repeated fractionation, a fraction (6 g) having the following constants was isolated: b.p. 104-105° at 3.5 mm; n_D^{20} 1.4268; d_4^{20} 0.9883.

Found %: P 16.09; 15.94
$C_8H_{19}O_3P$. Calculated %: P 15.97

From the higher fractions dihexylphosphorous acid was obtained: b.p. 138-141° at 3.5 mm; n_D^{20} 1.4332.

Preparation of (Ethyl)-octylphosphorous Acid

The amounts taken were: diethylphosphorous acid 15 g, octyl alcohol 14 g. 6 ml of alcohol was distilled off. Fractionation yielded the following fractions:

Fraction 1, b.p. 64-129° at 6mm – 6 g
Fraction 2, b.p. 129-155° at 7 mm – 7 g
Fraction 3, b.p. 155-200° at 7 mm – 10 g

After further fractionation there were isolated: diethylphosphorous acid, b.p. 61-62° at 7 mm; dioctylphosphorous acid, b.p. 191-194° at 6.5 mm; and (ethyl)-octylphosphorous acid, b.p. 126-128.5° at 4.5 mm; n_D^{20} 1.4312; d_4^{20} 0.9779.

Found %: P 14.22
$C_{18}H_{39}O_3P$. Calculated %: P 13.89

During each distillation, a readily volatile fraction (diethylphosphorous acid) and a fraction corresponding to dioctylphosphorous acid were separated.

SUMMARY

1. Viscosity determinations on dialkylphosphorous acids in dilute carbon tetrachloride or benzene solution give values of η_{equiv} that indicate that these substances are in the monomeric condition.

2. By transesterification of diethylphosphorous acid by the appropriate alcohol the following substances have been synthesized for the first time: dinonyl-, didecyl-, dihexadecyl-, bis(β-phenylethyl)-, (ethyl)hexyl-, and (ethyl)octyl-phosphorous acids.

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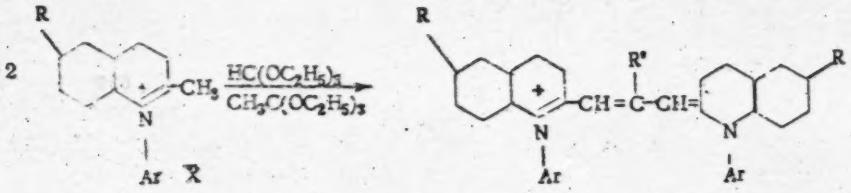
CYANINE DYES

COMMUNICATION 1. SYMMETRICAL N-ARYLQUINOCYANINES

G. T. Pilyugin

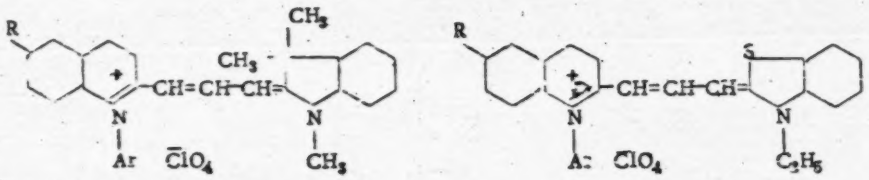
As we have already shown [1], when secondary aromatic amines react with paraldehyde, cyclization occurs with formation of a pyridine ring, and quinaldine derivatives having an aryl radical on the hetero nitrogen atom are obtained. Having thus prepared such aryl-substituted quinaldine derivatives for the first time, we succeeded in converting them, concurrently with cyclization, into the corresponding quaternary salts, which, owing to the presence of a reactive methyl group in the α-position, are susceptible to many chemical changes. As a result we have the prospect of preparing new organic compounds of various classes having the most varied properties. Our quaternary quinolinium salts with aryl radicals on the hetero N have been subjected to the cyanine condensation, yielding carbocyanines of symmetrical and of unsymmetrical structure.

Thus, by condensation of a N-arylquinolinium salt with orthoformic or orthoacetic ester, symmetrical dyes are obtained according to the scheme [2]:



where Ar = C_6H_5; $C_6H_4CH_3$(o,p); $C_{10}H_7$(α,β); R = CH_3, R' = H, CH_3; X = I, ClO_4.

When the quaternary salts react with 1,3,3-trimethyl-2-(2-N-phenylacetamidovinyl)-3H-pseudoindolium iodide or with 3-ethyl-2-(2-N-phenylacetamidovinyl)-benzothiazolium iodide, unsymmetrical carbocyanines are obtained [3]:



In this paper we shall examine the symmetrical carbocyanines that we have prepared. They are given in the following table.

It must be pointed out that the aryl radical on the hetero N considerably activates the α-methyl group; this is confirmed by the readiness with which the trinuclear quaternary salts undergo the cyanine condensation, even in the form of halides (but not arylsulfonates), which do not give the cyanine condensation at all when there is an alkyl on the hetero N. Also, the high reactivity is confirmed by the fact that the quinocyanine condensation occurs with orthoacetic ester; this is not so when there is an alkyl radical on the hetero N. This increased reactivity may be explained by the change resulting in the mutual electronic effects between the α-methyl and the radical on the hetero N when the latter is changed from alkyl to aryl.

It can be seen from the absorption spectra obtained that the introduction of methyl or of a fused benzene ring in various positions in the dye molecule leads to various bathochromic shifts in the absorption maximum, the effect being relatively great when the groups are introduced at some point in the benzene ring of the molecule, and considerably less when they are introduced into the grouping attached to the hetero nitrogen. Thus, the methyl group introduced symmetrically in the 6,6'-positions displaces the absorption maximum of the dye towards

TABLE

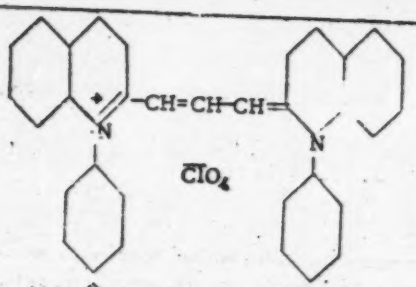
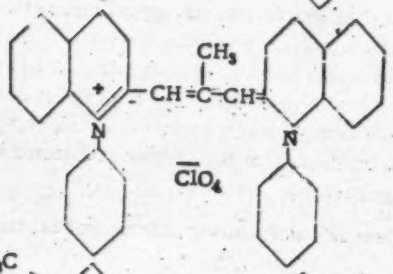
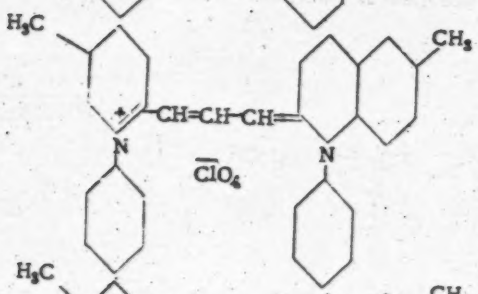
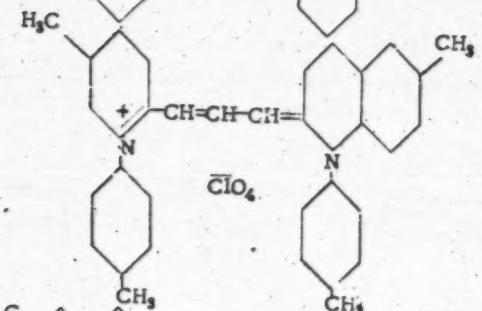
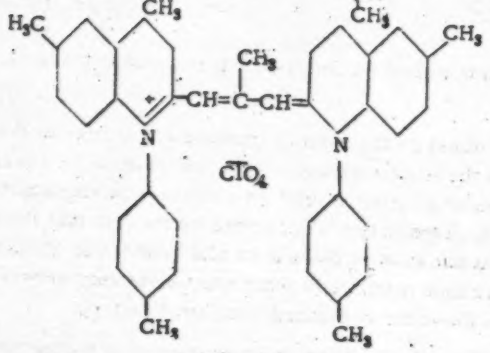
No.	Formula of dye	Absorption maximum (mμ)
1		614
2		610
3		620
4		622
5		618

TABLE (Continued)

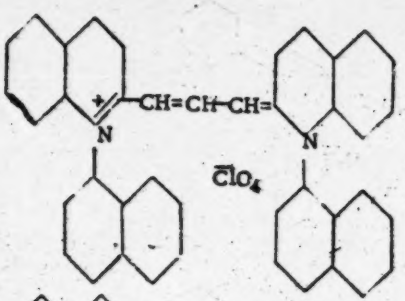
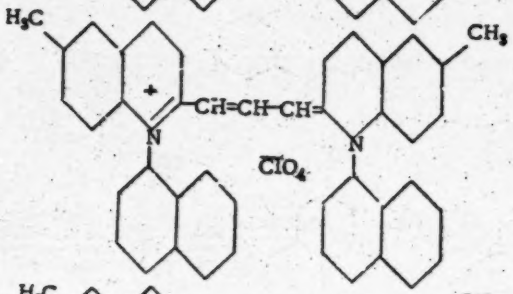
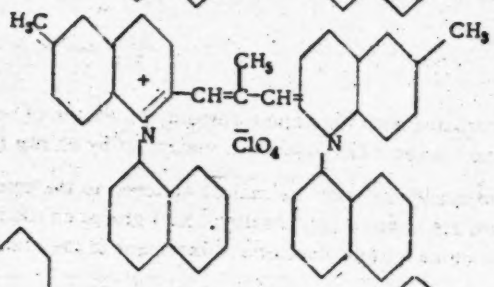
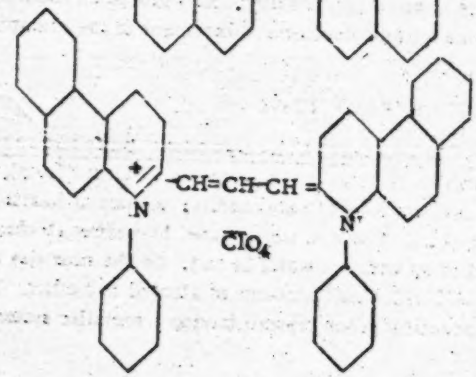
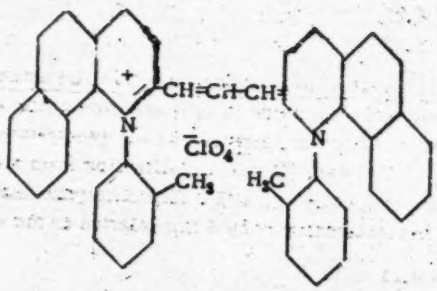
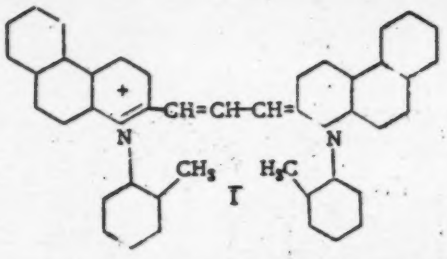
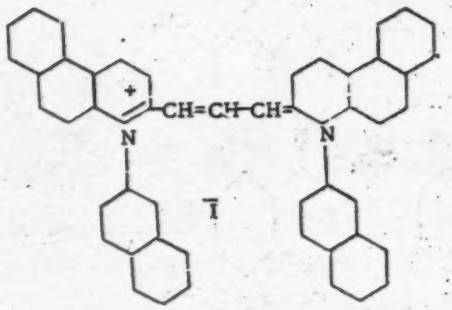
No.	Formula of dye	Absorption maximum (mμ)
6		618
7		625
8		620
9		645
10		642

TABLE (Continued)

No.	Formula of dye	Absorption maximum (mμ)
11		644
12		654

the red end of the spectrum by 6 mμ (compared with the unsubstituted dye). Fusion of benzene rings at the 5,6- and 5',6'-positions in the symmetrical dye displaces the absorption maximum by 31 mμ (dyes 1 and 9).

When similar substituents are introduced into the radical attached to the hetero nitrogen, the bathochromic shifts in the absorption maximum are considerably smaller. Aryl groups on the hetero nitrogen, when compared with alkyl groups, are found to cause a bathochromic displacement in the absorption maximum of the cyanine dye molecule.

EXPERIMENTAL

1. Bis-2-(1-phenylquinoline)-trimethinecyanine perchlorate. 1-Phenylquinaldinium perchlorate (1 g) and ethyl orthoformate (1 g) were condensed in pyridine (1.5 g), the mixture being boiled gently under reflux for 20 min. The dye was formed very readily: as soon as heating was commenced, the reaction mixture took on an intense blue color. The dye was isolated by adding alcohol (4 ml) to the pyridine solution, heating to the boil, and diluting with hot water (4 ml). On the next day the precipitated dye was filtered off and then washed with water and with small amounts of alcohol and ether. The dye, purified by recrystallization from alcohol, consisted of beautiful green crystals having a metallic luster, m.p. 276° (decomp.), absorption max. 614 mμ (0.2 g, 25%).

Found %: Cl 6.21

$C_{33}H_{25}N_2O_4Cl$. Calculated %: Cl 6.46

2. [Bis-2-(1-phenylquinoline)]-β-methyltrimethinecyanine perchlorate. 1-Phenylquinaldine perchlorate (1.5 g) was dissolved in pyridine (3 ml), and orthoacetic ester (3 g) was added. The mixture was boiled gently for 3 hrs. It was then cooled, and the dye was precipitated by means of ether, filtered off, and washed with ether and alcohol. The dye, after recrystallization from alcohol, was a dark-blue powder having a metallic luster, m.p. 231° (decomp.) (0.46 g, 18%). The absorption maximum of the dye in ethanol solution is at 610 mμ, i.e. displaced hypsochromically by 4 mμ relative to the unsubstituted dye.

Found %: Cl 6.11

$C_{34}H_{27}N_2O_4Cl$. Calculated %: Cl 6.30

3. Bis-2-(6-methyl-1-phenylquinoline)trimethinecyanine perchlorate. 2,6-Dimethyl-1-phenylquinolinium perchlorate (0.3 g), orthoformic ester (1 ml), and pyridine (1.5 g) were boiled together in a flask under reflux for 50 min. The mixture was cooled, and the dye formed was precipitated by ether and dissolved in a small amount of alcohol. On the next day the dye was filtered off and washed with alcohol and ether. The dye, after recrystallization from alcohol, was a finely crystalline dark-blue powder, m.p. 270° (0.1 g, 38.4%). Absorption maximum 620 mμ.

Found %: Cl 5.90

$C_{35}H_{33}N_2O_4Cl$. Calculated %: Cl 6.15

4. Bis-2-(6-methyl-1-p-tolylquinoline)trimethinecyanine perchlorate. 2,6-Dimethyl-1-p-tolylquinolinium perchlorate (0.5 g) was dissolved in pyridine (3 ml), ethyl orthoformate (0.25 g) was added, and the mixture was heated at the boil for 1 hr. As heating proceeded, the reaction mixture acquired an intense blue color. On the next day the precipitated crystals were filtered off and washed with alcohol and ether. The dye was obtained, after recrystallization, in the form of dark-green crystals having a metallic luster, m.p. 302° (0.16 g, 36.3%). Absorption maximum 622 mμ.

Found %: Cl 5.98

$C_{37}H_{32}N_2O_4Cl$. Calculated %: Cl 5.87

5. [Bis-2-(6-methyl-1-p-tolylquinoline)]-8-methyltrimethinecyanine perchlorate. The quaternary salt (0.4 g) was dissolved in pyridine (3 ml), and orthoacetic ester (0.25 g) was added. The mixture was boiled for 2 hrs and became progressively more intense in color. The dye was precipitated with ether, filtered off, dissolved in a small amount of alcohol, and precipitated with a saturated solution of potassium chlorate, the solutions of dye and of perchlorate being first brought to the boil. A small amount of water was added and the solution was boiled. When the solution was cooled, the dye precipitated and was then filtered off and washed with ether. It was recrystallized from aqueous alcohol. The dye contained (0.1 g, 20%) melted at 210° (decomp.). Absorption maximum 618 mμ, i.e. displaced relative to that of the unsubstituted dye by 4 mμ towards the short waves.

Found %: Cl 5.28

$C_{38}H_{35}N_2O_4Cl$. Calculated %: Cl 5.74

6. Bis-2-(1-(1-naphthyl)quinoline)trimethinecyanine perchlorate. 1-(1-Naphthyl) quinaldinium perchlorate (0.2 g), orthoformic ester (1 ml), and pyridine (2 ml) were boiled together for 40 min. The mixture was cooled, and the dye that had formed was precipitated by addition of ether (5 ml); it was dissolved in alcohol (2 ml) and left until the next day, when it was filtered off and washed with water, alcohol, and ether. The dye, after recrystallization from aqueous alcohol, was in the form of a finely crystalline dark-blue powder having a metallic luster, m.p. 235° (0.09 g, 25.4%). Absorption maximum 618 mμ.

Found %: Cl 5.28

$C_{41}H_{33}N_2O_4Cl$. Calculated %: Cl 5.47

7. Bis-2-(6-methyl-1-(1-naphthyl)quinoline)trimethinecyanine perchlorate.

The quaternary salt (0.4 g), orthoformic ester (0.2 ml), and pyridine (3 ml) were placed in a flask and boiled for 50 min. The contents of the flask gradually acquired a blue color. The dye was precipitated with ether, dissolved in a small amount of alcohol, and then precipitated by means of a saturated solution of potassium perchlorate. The dye, after recrystallization from aqueous alcohol, melted at 238° (decomp.) (0.15 g, 46%). Absorption maximum 625 mμ.

Found %: Cl 5.08

$C_{43}H_{35}N_2O_4Cl$. Calculated %: Cl 5.24

8. [Bis-2-(6-methyl-1-(1-naphthyl)quinoline)]-8-methyltrimethinecyanine perchlorate. The quaternary salt (0.25 g), orthoacetic ester (0.15 g), and pyridine (2 ml) were introduced into a 25 ml flask fitted with a reflux condenser. The mixture was gently boiled and given moderate shaking for 1 hr. A further amount (0.5 ml) of orthoacetic ester was then added to the reaction mixture, and heating was continued for a further 50 min. The contents were cooled, treated with ether, and dissolved in a small amount of alcohol. A saturated solution of potassium perchlorate (2 ml) was added to the hot alcoholic solution. The precipitated finely crystalline blue dye was filtered off and washed with ether and alcohol. The dye, after

recrystallization from aqueous alcohol melted at 210° (decomp.) (0.1 g, 48%). Absorption maximum 620 mμ.

Found %: Cl 4.87
$C_{44}H_{38}N_2O_4Cl$. Calculated %: Cl 5.14

9. Bis-3-(4-phenylbenzo/f/quinoline)trimethinecyanine perchlorate. 3-Methyl-4-phenylbenzo/f/quinolinium perchlorate (0.2 g), orthoformic ester (0.1 g), and pyridine (3 ml) were boiled together for 40 min with continuous shaking. As heating proceeded, the reaction mixture acquired a green color. When the mixture was cooled, beautiful dark-green crystals of the dye were precipitated. They were recrystallized from aqueous alcohol (0.06 g, 41%). The m.p. of the dye was 267° (decomp). Absorption maximum 645 mμ.

Found %: Cl 5.31
$C_{41}H_{29}N_2O_4Cl$. Calculated %: Cl 5.47

10. Bis-2-(1-o-tolylbenzo/h/quinoline)trimethinecyanine perchlorate. 2-Methyl-1-o-tolylbenzo/h/quinolinium perchlorate (0.2 g), orthoformic ester (0.1 g), and pyridine (3 ml) were boiled together for 1 hr. A green color developed and became more and more intense as heating continued. The solution was cooled, and the dye was precipitated with ether, filtered off, dissolved in a small amount of alcohol, and left to stand until the next day. The precipitated dye was filtered off and washed with water, alcohol, and ether. The dye, after recrystallization from aqueous alcohol melted at 287° (decomp.) (0.08 g, 37%). Absorption maximum 642 mμ.

Found %: Cl 5.08
$C_{45}H_{33}N_2O_4Cl$. Calculated %: Cl 5.24

11. Bis-3-(4-o-tolylbenzo/f/quinoline)trimethinecyanine iodide. 3-Methyl-4-o-tolylbenzo/f/quinolinium iodide (0.2 g), orthoformic ester (1 ml), and pyridine (1 ml) were boiled and shaken continuously for 30 min. When heating was applied, the mixture at first darkened; it then took on a greenish tinge, and by the end of the heating period it had acquired an intense green color. The dye was precipitated with ether and dissolved in a small amount of alcohol. On the next day the precipitated dye was filtered off and washed with alcohol and ether. The dye, after recrystallization from aqueous alcohol, melted at 287° (decomp. (0.038 g, 22%). Absorption maximum 644 mμ.

Found %: I 17.88
$C_{43}H_{33}N_2I$. Calculated %: I 18.03

12. Bis-3-(4-(2-naphthyl)benzo/f/quinoline)trimethinecyanine iodide. 3-Methyl-4-(2-naphthyl)benzo/f/quinolinium iodide (0.4 g), pyridine (2 ml), and orthoformic ester (0.2 g) were boiled gently together for 20 min. As heating proceeded the reaction mixture gradually acquired a bright green color. The mixture was cooled, and the dye was precipitated by addition of ether. The dye powder was filtered off, washed with alcohol and ether, and recrystallized from aqueous alcohol. The dark-green dye melted, after recrystallization, at 275-278° (21% yield). Absorption maximum 654 mμ.

Found %: I 16.13
$C_{49}H_{33}N_2I$. Calculated %: I 16.36

I express my sincere thanks to V. N. Tolmachev, senior scientific worker in the Institute of Chemistry of the Kharkov State University, for help in the determination of absorption spectra.

SUMMARY

1. Starting from N-arylquinolinium salts, twelve new symmetrical carbocyanines having phenyl and naphthyl radicals on the hetero nitrogen have been prepared.

2. It has been shown that the introduction of phenyl and naphthyl radicals on the hetero nitrogen of quinocarbocyanines causes a bathochromic shift in the absorption maximum, as compared with the N-ethyl compounds, of 10-12 and 14-18 mμ respectively.

3. Introduction of a methyl group in the meso-position of the polymethine chromophore of N-aryl-carbocyanines causes an insignificant hypsochromic shift of the absorption maximum, as compared with the unsubstituted compounds.

4. The presence of aryl radicals on the hetero nitrogen of quinolinium salt increases the activity of the 2-methyl group. This is confirmed by the readiness with which complex quaternary halides undergo cyanine condensations.

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* See Consultants Bureau translation, p. 347.

CYANINE DYES

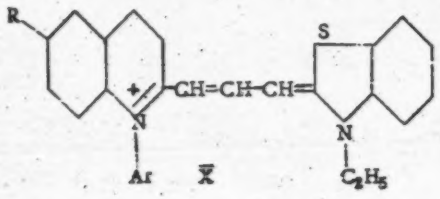
COMMUNICATION 2. UNSYMMETRICAL CARBOCYANINES FROM DERIVATIVES OF N-ARYLQUINALDINE AND OF BENZOTHIAZOLE

G. T. Pilyugin

Symmetrical quinocyanines were among the first of the cyanine dyes [1]. Also, they were among the first of the cyanine group to be examined for sensitization purposes. However, as this question developed they became displaced by thiacyanines [2], which were found to be more powerful as sensitizers than quinoline derivatives.

At the present time, among all the classes of sensitizing dyes, it is the thiacyanine class that receives the most study and is to be assigned the leading place. The position occupied by the thiacyanine dyes is reflected in the relevant journal, patent, and monographic literature. However, this applies only to the various types of symmetrical thiacyanine, in which identical basic residues derived from thiazole are to be found at the ends of the polymethine chain. With regard to the unsymmetrical quinothiacyanines, they form the subject of a relatively few sporadic investigations. This is to be attributed to the fact that they are much more difficult to synthesize than the symmetrical dyes.

Kipriianov and Pilyugin have described a number of quinothiacyanines prepared from a benzothiazole intermediate product in conjunction with quinoline derivatives [3]. Unsymmetrical dyes containing a quinoline system having an aryl radical on the hetero nitrogen have been hitherto unknown in chemistry and are described by us for the first time [4]. In this group of quinothiacyanines of general formula



where Ar = C_6H_5; $C_6H_4CH_3$ (o,p); $C_{10}H_7$ (α,β); X = ClO_4, I, we have synthesized a number of dyes. A study of the effect of the aryls attached to the hetero nitrogen atom on the color of the unsymmetrical quinothiacarbocyanines presented some interest.

The structures of the unsymmetrical dyes that we have synthesized are presented in the table, where there are given also the optical data for the corresponding symmetrical dyes.

Introduction of phenyl in place of ethyl on the hetero nitrogen atom of an unsymmetrical quinothiacarbocyanine resulted in a shift in the absorption maximum towards the red end of the spectrum of 6.5 mμ. Introduction of a methyl group into the unsymmetrical molecule resulted in an insignificant bathochromic shift (1-2 mμ, No. 2 and 3). The presence of a methyl group in the benzene nucleus and, simultaneously, of a fused benzene ring in the substituent on the hetero nitrogen atom caused a bathochromic shift of 8 mμ in the absorption maximum (No. 4).

As has been noted previously, fusion of the same ring on the benzene nucleus leads to a bathochromic shift in the absorption maximum of 8-11 mμ (No.5,6,8), while fusion to the substituent on the hetero nitrogen leads to a considerably smaller shift (4 mμ). The simultaneous addition of two fused benzene rings to the molecule, one on the benzene nucleus and one on the substituent at the hetero nitrogen, leads to a shift of 14 mμ towards the longer waves.

EXPERIMENTAL

[2-(1-Phenylquinoline)][2-(3-ethylbenzothiazole)] trimethinecyanine perchlorate. 3-Ethyl-2-(2-N-phenylacetamidovinyl)benzothiazolium iodide (0.52 g), 1-phenylquinaldinium perchlorate (0.35 g),

TABLE

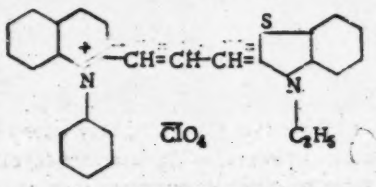
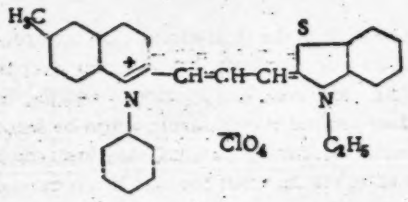
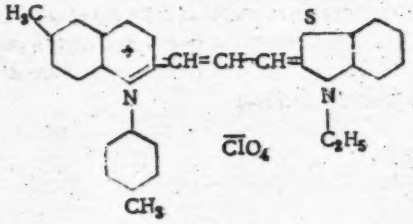
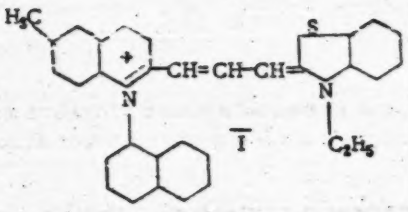
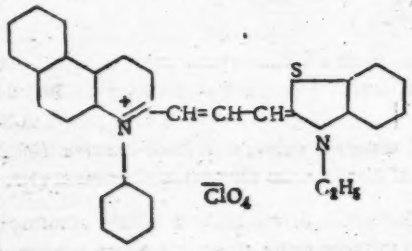
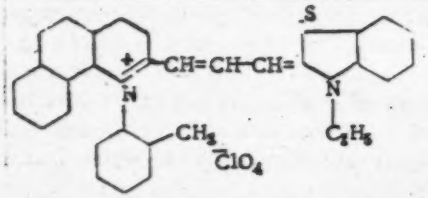
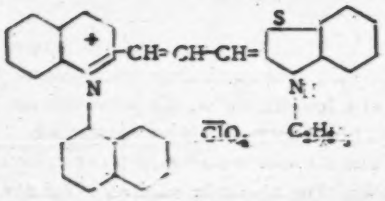
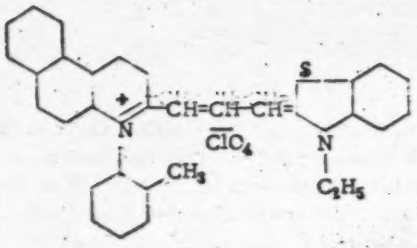
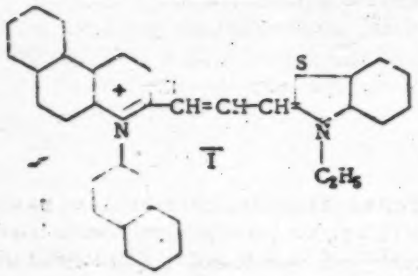
No.	Formula of dye I / II	Absorption max. (mμ) Sym-metrical from I	Sym-metrical from II	Unsym-metrical calcd. $\frac{I+II}{2}$	Unsym-metrical (found)	Shift from additive: hypso-chromic	Shift from additive: batho-chromic	$E_{max} \cdot 10^{-4}$
1		614	558	586	586	–	–	13.1
2		620	558	589	587	2	–	13.3
3		622	558	590	588	2	–	13.9
4		625	558	591.5	594	–	2.5	13.7
5		645	558	601.5	596	5.5	–	14.8

TABLE (Continued)

No.	Formula of dye I	II	Absorption max. (mμ) Symmetrical from I	Symmetrical from II	Unsymmetrical calcd. $\frac{I+II}{2}$	Unsymmetrical (found)	Shift from additive hypsochromic	Shift from additive bathochromic	$\varepsilon_{max} \cdot 10^{-4}$
6			642	558	600	597	3	—	13.2
7			618	558	588	590	—	2	12.2
8			644	558	601	594	7	—	13.8
9			654	558	606	600	6	—	14.2

and pyridine (2 ml) were boiled together for 40 min. The dye was precipitated from the pyridine solution with aqueous alcohol and was purified by recrystallization from alcohol. Glistening blue needles (0.2 g, 42.54%), m.p. 256-257° (decomp.). Absorption maximum 586 mμ.

Found %: Cl 7.25

$C_{27}H_{25}N_2ClO_4$. Calculated %: Cl 6.99

[2-(6-Methyl-1-phenylquinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. The quaternary salt from 2,6-dimethyl-1-phenylquinoline (0.2 g) and the 2-methylbenzothiazole intermediate product (0.24 g) were placed in a 25-ml flask, and pyridine (3 ml) and a few drops of acetic anhydride

were added. The contents of the flask were heated for 40 min with frequent shaking. The mixture was cooled, and the dye was precipitated with ether and dissolved in a small amount of alcohol. The dye precipitated from the cooled solution; it was filtered off and washed with alcohol and ether. Recrystallization yielded a dark-blue crystalline powder having a metallic luster (0.09 g, 34.6%), m.p. 270° (decomp). Absorption maximum of the dye: 587 mμ.

Found %: Cl 7.72
$C_{28}H_{25}N_2ClO_4$. Calculated %: Cl 7.64

[2-(6-Methyl-1-p-tolylquinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. The quaternary salt (0.4 g, 1.2 mol), the 2-methylbenzothiazole intermediate product (0.4 g, 1 mol), and pyridine (3 ml) were placed in a flask fitted with a reflux condenser and were boiled together continuously for 40 min. The dye was precipitated with ether and then dissolved in alcohol (1 ml). Crystallization was induced by scratching with a glass rod; the crystals were filtered off and washed with alcohol and ether. The dye, after recrystallization from aqueous alcohol, melted at 232-234° (decomp.) (0.2 g, 35%). Absorption maximum of dye: 588 mμ.

Found %: Cl 6.10
$C_{29}H_{27}N_2ClO_4$. Calculated %: Cl 6.45

[2-(6-methyl-1-(1-naphthyl)quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine iodide. 2,6-Dimethyl-1-(1-naphthyl)quinolinium iodide (0.25 g), the benzothiazole intermediate product (0.15 g), and pyridine (2 ml) were heated together with addition of a few drops of acetic anhydride for 40 min under reflux. On boiling, the reaction mixture took up a stable bluish-violet color. The mixture was cooled and treated with ether. The precipitate was dissolved in alcohol, and the solution obtained was left overnight. The fine crystals that formed were filtered off and washed with ether. The alcoholic solution of the dye is bluish violet. The dye, after recrystallization from aqueous alcohol, melted at 233° (decomp.) (0.06 g, 38%). Absorption maximum of the dye: 594 mμ.

Found %: I 20.88
$C_{32}H_{27}N_2I$. Calculated %: I 21.23

[3-(4-Phenylbenzo/f/quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. 3-Methyl-4-phenylbenzo/f/quinolinium perchlorate (0.22 g), the 2-methylbenzothiazole intermediate product (0.16 g), pyridine (2 ml), and a few drops of acetic anhydride were boiled together for 1 hr with frequent shaking. The mixture was cooled and the unsymmetrical dye was precipitated by addition of a small amount of ether. It was dissolved in alcohol (2 ml) and precipitated by addition of a saturated solution of potassium perchlorate followed by addition of water (10 ml) and boiling. The finely crystalline precipitate of dye was filtered off, washed with ether, alcohol, and water, and recrystallized from aqueous alcohol (0.09 g, 32%). The cyanine condensation was repeated several times in order to obtain sufficient dye for further investigations. The dye had a m.p. of 220° (decomp) and absorption maximum of 596 mμ.

Found %: Cl 6.19
$C_{31}H_{25}N_2ClO_4$. Calculated %: Cl 6.37

[2-(1-o-Tolylbenzo/h/quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. 2-Methyl-1-o-tolylbenzo/h/quinolinium perchlorate (0.3 g), the 2-methylbenzothiazole intermediate product (0.15 g), pyridine (3 ml), and a few drops of acetic anhydride were placed in a flask fitted with reflux condenser and boiled together over an asbestos gauze for 50 min. As heating continued, the bluish-lilac color of the reaction mixture became more and more intense. When the mixture was cool, the dye did not come out in a crystalline form, and it was therefore precipitated by addition of a small amount of ether. The precipitate formed was dissolved in alcohol (1 ml) to which, at the boil, a saturated solution of potassium perchlorate was added. The finely crystalline dye was filtered off and washed with water, alcohol, and ether. The dye was recrystallized from aqueous alcohol (0.1 g, 22%). It had m.p. 227° (decomp) and absorption maximum 597 mμ.

Found %: Cl 6.08
$C_{32}H_{27}N_2ClO_4$. Calculated %: Cl 6.22

[2-(1-(1-Naphthyl)quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. 1-(1-Naphthyl)quinaldinium perchlorate (0.2 g), the 2-methylbenzothiazole intermediate product (0.24 g), pyridine (3 ml), and acetic anhydride (2 drops) were placed in a flask and heated at the boil

over an asbestos gauze for 40 min. When the solution had cooled, the dye was separated by addition of ether (5 ml); it was filtered off and was recrystallized from aqueous alcohol (0.08 g, 32.2%). The dye is a dark-blue crystalline powder having a metallic luster, m.p. 228° (decomp). The absorption maximum of the dye is 590 mμ.

Found %: Cl 6.22

$C_{31}H_{25}N_2ClO_4$. Calculated %: Cl 6.37

[3-(4-o-Tolylbenzo/f/quinoline)][2-(3-ethylbenzothiazole)]trimethinecyanine perchlorate. 3-Methyl-4-o-tolylbenzo/f/quinolinium iodide (0.2 g), 3-ethyl-2-(N-phenylacetamidovinyl)-benzothiazolium iodide (0.15 g), pyridine (2.5 ml), and acetic anhydride (2 drops) were heated together at the boil for 50 min in a flask fitted with reflux condenser. When the mixture had cooled, the dye was precipitated with ether and then dissolved in alcohol (2 ml); a saturated solution of potassium perchlorate (2 ml) was added, and the mixture was heated to the boil. On the next day the finely crystalline precipitate of dye was filtered off, washed with ether and alcohol, and recrystallized from aqueous alcohol (0.085 g, 31.4%). The dye was in the form of dark-violet crystals having a metallic luster, m.p. 215°. Absorption maximum 594 mμ.

Found %: Cl 6.16

$C_{35}H_{27}N_2ClO_4$. Calculated %: Cl 6.22

[3-(4-(2-Naphthyl)benzo/f/quinoline)][2-(3-ethylbenzothiazole)]trimethine-cyanine iodide. The benzothiazole intermediate product (0.4 g), the quaternary salt (0.49 g), pyridine (2 ml), and acetic anhydride (0.5 ml) were placed in a flask fitted with reflux condenser and boiled gently for 40 min. As heating proceeded, the contents of the flask acquired a bluish-green color with a reddish tinge. When the mixture had cooled, the dye was precipitated with ether and filtered off after being converted into the solid state by intermediate dissolution in a small amount of alcohol. The dye was recrystallized from aqueous alcohol (0.22 g, 40.7%). M.p. 250° (decomp.). The absorption curve of a solution of the dye in ethanol was determined; absorption maximum: 600 mμ.

Found %: I 19.88

$C_{35}H_{27}N_2I$ Calculated %: I 20.03

I express my sincere thanks to V. N. Tolmachev, senior scientific worker in the Institute of Chemistry of the Kharkov State University, for help in the determination of absorption spectra.

SUMMARY

1. Nine new quinothiacarbocyanines have been prepared containing aryl radicals on the hetero nitrogen of quinoline.

2. It has been shown that replacement of ethyl on the hetero nitrogen atom by phenyl or naphthyl leads to a slight bathochromic shift in the absorption maximum of the dye.

3. The absorption maxima of the quinothiacarbocyanines obtained may be derived by an additive relationship from those of the corresponding symmetrical dyes, but the intensity of the absorption is reduced in comparison with that of the corresponding symmetrical dyes.

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* See Consultants Bureau English Translation, p. 347.

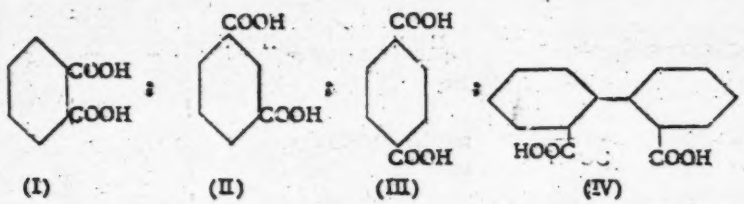
MACROMOLECULAR COMPOUNDS

COMMUNICATION 44. POLYESTERS OF CERTAIN AROMATIC DICARBOXYLIC ACIDS

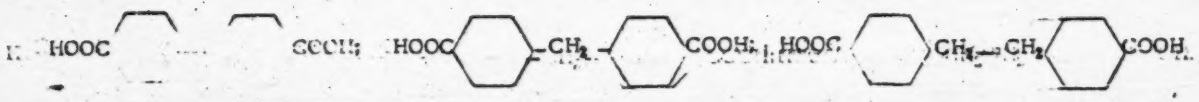
V. V. Korshak and T. A. Soboleva

Polyesters derived from glycols and aromatic dicarboxylic acids have as yet received very little investigation. There are only a few papers in the literature that are devoted to the study of such compounds [1]. Thus, Drinberg, Snedze, and Nechaeva [2] studied the polycondensation of diphenic acid with glycerol and described the properties of the polyesters formed. Polyethylene diphenate was described also by Carothers and Arvin [3].

The object of the present investigation was to determine the effect on the properties of the polyester of the structure of the aromatic dicarboxylic acid, particularly with respect to the relative positions of the carboxyl groups and to the number of aromatic nuclei, and to elucidate also the part played by the methylene groups separating these nuclei. For this purpose we have prepared polyesters by the condensation of glycols (ethylene glycol and diethylene glycol) with aromatic dicarboxylic acids having either one nucleus, e.g. phthalic (I), isophthalic (II), terephthalic (III), or two nuclei: diphenic (IV) and 4,4'-biphenyldicarboxylic (V). Also, acids having one or two methylene groups situated between aromatic nuclei were taken: 4,4'-methylenedibenzoic acid (VI) and α,α'-bi-p-toluic acid (VII):



(I) (II) (III) (IV)



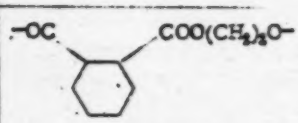
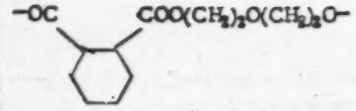
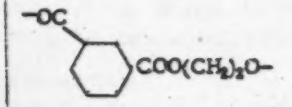
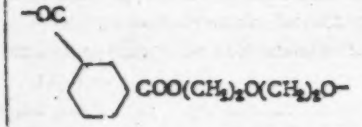
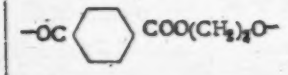
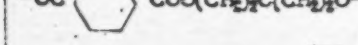
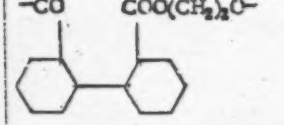
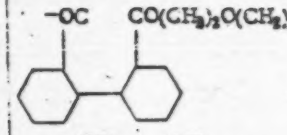
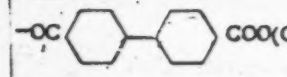
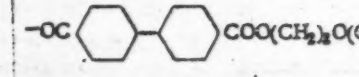
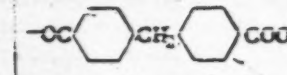
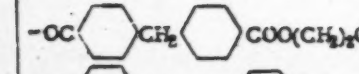
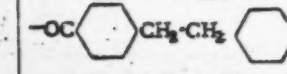
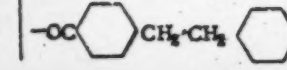
(V) (VI) (VII)

From these acids a number of polyesters were prepared. Their properties are given in the table.

In solvents such as acetic acid, acetone, strong hydrochloric acid, and aqueous caustic soda all the polyesters enumerated in the table are insoluble with the exception of the ethylene glycol and diethylene glycol esters of diphenic acid, which dissolve in hot acetic acid. As will be seen from the table, the properties of the polyesters vary in regular fashion when one glycol or acid is changed for another. All the ethylene glycol esters are solids having melting points higher than those of the diethylene glycol esters. The latter are sometimes liquid at room temperature, (polyester of phthalic acid) or are rubberlike (polyester of terephthalic acid). In this case there is manifested the specific effect of the ether linkage in the diethylene glycol residue; this confers a high flexibility on the polyester chain, which is expressed in the lower melting point and in the appearance of rubberlike properties. That the cause in this case is the ether linkage may be shown by a comparison of polydiglycol terephthalate with polypentamethylene terephthalate [4].

The effect of the structure of the dicarboxylic acid on the properties of the polyester is still greater. Thus, in the case of the isomeric benzenedicarboxylic acids the properties of the polyesters change fundamentally with change in the relative positions of the carboxyl groups. As we proceed in order from the ortho to the meta and para isomers, the melting point rises both for the ethylene glycol polyesters (92-104, 102-108, 250-256° respectively)

TABLE

No.	Repeating unit	Appearance of polyester	M.p. °C	Solubility in					
				dioxane	chloroform	alcohol	benzene	cresol	sulfuric acid
1		solid	92-104	x	x	–	–	+	+
2		like petroleum jelly	sirup	x	x	–	x	+	+
3		solid	102-108	–	–	–	–	x	+
4		"	85-90	–	–	–	–	x	+
5		"	256	–	–	–	–	x	x
6		rubber-like	125-139	–	+	–	–	x	x
7		brittle solid	110-130	x	x	–	x	x	+
8		solid	80-95	–	–	–	x	x	+
9		"	not melted below 320°	–	–	–	–	–	x
10		"	159-170	–	–	–	–	x	x
11		"	not melted below 320°	–	–	–	–	–	x
12		"	126-145	x	x	–	–	x	x
13		"	not melted below 320°	–	–	–	–	–	x
14		"	85-105	–	–	–	–	x	x

NOTE. The sign – indicates insoluble, + indicates soluble at room temperature

and for the diethylene glycol polyesters (like petroleum jelly, 85-90, 125-139° respectively). It is interesting to note that a similar picture is to be observed also for the biphenyldicarboxylic acids: the polyesters of the para acid melt higher than the polyesters of the ortho acid, both for ethylene glycol (m.p. 110-130° and above 320° respectively), and also for diethylene glycol (m.p. 70-85° and 159-170° respectively).

Also, the effect should be noted of the number of benzene nuclei and of their relative disposition. Polyesters from a biphenyldicarboxylic acid have higher melting points than polyesters from the corresponding benzenedicarboxylic acids. Thus for the polyesters from ortho- and para-dicarboxylic acids and a) ethylene glycol the melting points are respectively 92-104° and 110-130° (benzenedicarboxylic), 250-256°, higher than 320° (biphenyldicarboxylic), while for the polyesters with b) diethylene glycol we have: sirup, m.p. 70-85° (benzenedicarboxylic), m.p. 125-139°, 159-170° (biphenyldicarboxylic). This is the picture when the phenyl groups adjoin.

If, however, dicarboxylic acids are taken in which the two phenyl groups are separated by one or by two methylene groups, the melting points of the polyesters are lowered in comparison with those of the biphenyldicarboxylic derivatives; thus in the case of the polyesters from diethylene glycol: m.p. respectively 159-170°, 126-145°, 85-105°

With regard to the effect of the structure of the acid on the solubility of the polyester, an equally clear picture is to be observed. The polyesters from diethylene glycol are generally more readily soluble than those from ethylene glycol. Polyesters from p-dicarboxylic acids are less soluble than those from m- or o-acids. Polyesters derived from dicarboxylic acids containing two benzene nuclei substituted in the p-positions are distinguished by particularly poor solubility. Some of them are soluble only in strong sulfuric acid on warming, when it is possible that hydrolytic breakdown takes place. In the other solvents they do not dissolve, being similar to three-dimensional polymers in this respect.

The Properties of Three-dimensional Polymers

Until comparatively recently it has been considered axiomatic that three-dimensional macromolecular compounds are distinguished from linear compounds of this type by their complete insolubility and inability to melt when heated [5]. We consider that the cause of these differences is that three-dimensional macromolecular compounds consist essentially of linear chains knit together by a greater or smaller number of cross-links. Owing to the presence of these chemical cross-links, the linear chains cannot be separated from one another either by solvation forces or by moderate thermal action, for the energies of these linkages are too great to be overcome by forces arising from the action of solvents or of moderate heating. Sometimes, if the number of cross-links is not high, swelling occurs in the three-dimensional structure owing to the intrusion of solvent between the polymer molecules. However, this swelling does not lead finally to dissolution, but amounts essentially to the absorption of a large amount of solvent. In the case of such three-dimensional polymers, moderate heating leads generally to softening, but not to melting.

Macromolecular compounds, both three-dimensional and linear, undergo destruction at high temperatures as a result of pyrolysis; this occurs when the energy of the thermal movements of the molecules begins to exceed the energies of the chemical bonds. However, such concepts and definitions are beginning to come more and more into conflict with the experimental facts. Quite a few macromolecular compounds have been synthesized recently which undoubtedly belong to the class of linear polymers, but have properties that are characteristic of three-dimensional compounds. Examples of such substances are to be found in the polyamides prepared by us from adipic or sebacic acid and diamines such as benzidine [6] or α,α'-bi-p-toluidine [7], also in the series of polyesters formed between ethylene glycol or diethylene glycol and aromatic dicarboxylic acids, described in this paper; also, polymers such as polyvinylidene chloride [8], polytetrafluoroethylene [9], and, probably, urea-formaldehyde resin [10].

In the molecules of these polymers, cross-links are absent, but the polymers are insoluble in all solvents and do not melt when heated (they decompose at high temperatures). Consequently, in their properties they correspond to three-dimensional compounds. The cause of this phenomenon is to be found in the large number of polar groups, such as amide or phenylene, and of such atoms as chlorine or fluorine that are contained in the macromolecules of the compounds enumerated. Also, their chains are notable for their tendency to become close-packed, which is expressed by an X-radiogram corresponding to a high content of orderly crystalline substance. Owing to the presence of these polar groups, the usually rather weak Van der Waals forces between the chains become considerable, and hence the binding force of one chain to another attains high values. The magnitude of

these forces, evidently, can in a number of cases attain the same value as the forces in the primary chemical of bonds in three-dimensional polymers. Hence, such macromolecular compounds acquire property that are typical for three-dimensional polymers: they do not dissolve and do not melt.

This conclusion is confirmed by the fact that when the amide hydrogen atoms of polyamides are replaced by methyl groups readily soluble rubberlike polyamides are obtained [11]; for the formation of hydrogen bonds between the individual polyamide chains, which determine the great force that binds the individual chains to one another, does not now occur. Another example is the copolymer of vinylidene chloride with vinyl chloride. In this copolymer, the residues of the two original substances are not disposed in a regular fashion, and it is difficult for an orderly arrangement to be attained. Hence, this copolymer dissolves and melts more readily than polyvinylidene chloride.

On the basis of the above we may conclude that absence of an ability to dissolve and to melt is not always a proof of a three-dimensional structure; it may be an attribute also of linear polymers when polar groups are present and there is a tendency to take up an ordered arrangement.

The polyesters that we have prepared from dicarboxylic acids containing two benzene nuclei are insoluble in all organic and inorganic solvents, apart from strong sulfuric acid. Thus, in this respect they resemble three-dimensional polymers. However, this resemblance is purely formal, for there is no doubt that we are concerned here with linear polymers. The reason for the lack of solubility is evidently connected with the presence of fairly high binding forces between the benzene nuclei of individual chains. As is well known, the benzene ring contains six π-electrons, which are distributed within the nucleus and are energetically not fully saturated; their orbitals are disposed perpendicularly to the plane of the ring, and it is evident that their interaction results in the appearance of large mutual forces between these nuclei.

SUMMARY

1. Polyesters have been prepared by the condensation of ethylene glycol and diethylene glycol with aromatic dicarboxylic acids.

2. The question of the effect of the structure of the polymer chain on the physical properties of the polymer has been examined.

3. It has been shown that generally held views concerning three-dimensional polymers require modification.

4. The properties of the polyesters obtained have been demonstrated.

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MACROMOLECULAR COMPOUNDS

COMMUNICATION 45. SIGNIFICANCE OF THE DECARBOXYLATION OF DICARBOXYLIC ACIDS IN THE POLYCONDENSATION PROCESS

V. V. Korshak and S. V. Rogozhin

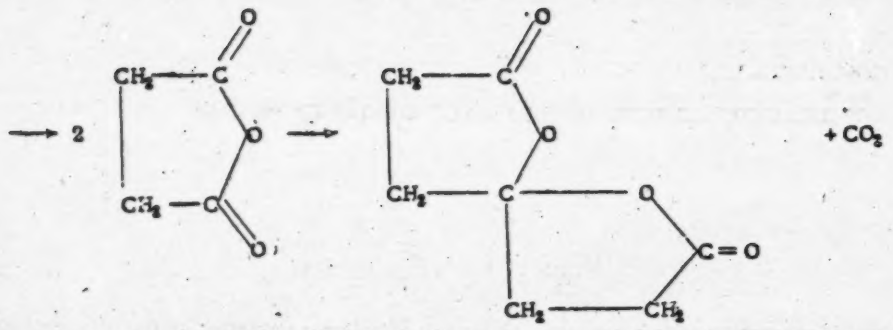
In the chemistry of macromolecular compounds the process of polymer formation by the polycondensation of bifunctional compounds is usually broken down into three fundamental stages: 1) beginning of chain growth, 2) chain growth, and 3) curtailment of chain growth.

The laws of the first two stages of the process have received a fair degree of study and development in a number of papers [1,2], but the causes leading to termination of chain growth have still not been fully elucidated. It has been found that, owing to the equilibrium nature of the polycondensation process, the molecular weight of the polymer, i.e., its chain length, is greatly affected by the ratio of components [3] and by the possibility of various chemical reactions at the terminal functional groups, leading to breaking of the chain [4].

The occurrence of chemical reactions at the terminal functional groups has been established in a number of investigations [5]. One of us with Zamyatina has observed that in the polycondensation of 1,6-hexanediamine with adipic acid the splitting-off of carbon dioxide from the adipic acid occurs [6]. The significance of such chemical changes, which lead to the destruction of the reacting end-groups, is particularly great in the preparation of linear polymers by condensation of bifunctional compounds. The determination of the effect of temperature on the thermal stability of dicarboxylic acids presents undoubted interest in connection with the possibility of decarboxylation during the course of polycondensation, but systematic investigations of this kind have not yet been carried out, and only isolated results are to be found in the literature. It is known, for example, that the presence in the molecule of a dicarboxylic acid of two carboxyl groups, which have a negative character, greatly increases the tendency to undergo decomposition. It is obvious that this effect will be most prominent among the first members of the homologous series of dicarboxylic acids owing to the mutual proximity of the carboxyl groups.

Actually, on being heated, oxalic acid yields carbon dioxide and formic acid [7]. It has been found that the reaction proceeds particularly rapidly at above 170°. The rate of decomposition increases in presence of water. Malonic acid decomposes more readily than oxalic acid. On being heated to 140°, malonic acid loses carbon dioxide and is converted into acetic acid [8]. This change occurs below 70° in aqueous solution [9]. The majority of the homologs of malonic acid decompose in the range 160-180°. When the fatty acids, and particularly their salts, are decomposed, ketones formed from the two acid residues are the main decomposition products. In the case of dicarboxylic acids, it is necessary to take into account the possibility of the formation of anhydrides and of cyclic ketones. Anhydride formation may proceed also by the splitting of water from two molecules of acid and may lead to formation of linear polyanhydrides of high molecular weight.

Investigations of Carothers and Hill [10] showed that in these reactions five- and six-membered rings were the most readily formed. When the structural unit contains 7-15 members, dimeric cyclic products or linear polymers are often formed. Thus, succinic acid, on being heated, readily forms an anhydride having a five-membered ring [11], which, on being heated further, is slowly converted by the splitting-off of one molecule of carbon dioxide from two molecules of the anhydride into the dilactone of γ-oxopimelic (hydrochelidonic) acid.



Glutaric acid rapidly distils with slight decomposition at below 300°. When it is distilled slowly, a mixture of acids and anhydrides is formed. Cyclopentanone is readily formed by the action of heat on salts of adipic acid. Aschan [12] found that cyclopentanone is formed when adipic acid is heated in presence of carbon dioxide. Blank [13] prepared cyclopentanone in 50% yield by heating adipic anhydride. Very little is known concerning the pyrolysis of the higher dicarboxylic acids. It is known that the presence of various catalysts greatly reduces the decomposition temperature.

EXPERIMENTAL

All the investigations reported in the literature on the decomposition of organic acids are based on chemical methods of investigating the decomposition products. In a number of investigations, the kinetics of decomposition have been determined from the change in the acid value [14], for which a considerable amount of substance, and also of time, is required for the performance of the investigation.

The method that we have developed presents the possibility of following continuously the course of the decomposition of acids, and an insignificant amount of material is required for the investigation. A weighed amount of the substance under investigation contained in a small tube is placed in a bath of Wood's metal. The tube is connected by narrow rubber tubing to a measuring system, which is contained in a thermostat; the temperature of the liquid in this thermostat is maintained constant within $\pm$ 0.05° by the aid of a Hoppler thermostat. The volume of the measuring system, tubing, and reaction tube is measured accurately. The gaseous decomposition products alter the pressure in the system, the changes in pressure being determined by the aid of the water and mercury manometers that form part of the measuring system. The course of the decomposition can be judged from the rate at which the pressure changes. The arrangement is shown diagrammatically in Figure 1. (See plate, page 547-a).

The calculation of the volume of carbon dioxide evolved and of the percentage decomposition of the acid under investigation is based on the excess pressure in the system, on the results of measurement of the volume of the system of manometric tubes, and on the fundamental law of the kinetic theory of gases:

$$\frac{p_0 V_0}{T_0} = \frac{p_1 V_1}{T_1}$$

The correctness of the formulas was verified by determining the percentage of decomposition of the acid by titration of the undecomposed acid. For all experiments on the decomposition of oxalic and malonic acids agreeing results were obtained.

The volume of carbon dioxide evolved was calculated for our experimental arrangement by the formulas:

$$\Delta V = \frac{273\Delta p}{760T}\left[V_0' + 0.01073\left(p_{at} + \frac{\Delta p}{13.6}\right)\right]$$

or

$$\Delta V = \frac{273\Delta' p}{760T}[V_0' + 0.146(p_{at} + \Delta' p)]$$

When the water manometer is cut out

$$\Delta V = \frac{273\Delta' p}{760T}[V_0' + 0.01(p_{at} + \Delta' p)],$$

where Δp is the excess pressure in mm water, $\Delta' p$ is the excess pressure in mm Hg, P_{at} is the atmospheric pressure in mm Hg., V_0' is the volume of the system (ml) at atmospheric pressure, T is the temperature of the thermostat liquid in °K.

The percentage decomposition of the acid is

$$2.232 \cdot 10^{-4}\frac{M \cdot \Delta V}{n},$$

where M is the molecular weight of the acid, ΔV is the volume of carbon dioxide evolved, and n is the amount of acid (g).

For monocarboxylic acids the coefficient is doubled.

EXPERIMENTAL PROCEDURE

A weighed amount (0.2-1.0 g) of the substance is placed in the tube, which is inserted into its jacket, through which water from the Höppler thermostat is flowing; in this way the temperature conditions throughout practically the whole of the reaction tube are made the same as those in the rest of the system. The tube is connected to the system with rubber tubing, and the tap that connects the whole system to the atmosphere is opened. The tube with its connecting tubing is placed in a thermostated vessel and kept there for 10 minutes; the temperature of the air in the system should then be equal to the temperature of the thermostat liquid. The tap connecting the system to the atmosphere is closed, and the reaction tube is placed in the bath of Wood's metal. The temperature of the bath is varied by the aid of a contact thermometer and a relay, or it is maintained constant within ±0.5°. At definite intervals of time at constant decomposition temperature, or at definite intervals of temperature when the temperature is varied, the excess pressure is read on the water manometer, if it is low, or on the mercury manometer, if it is high. When decomposition is complete, the tube is again placed in the thermostat and kept there for 10 minutes. The excess pressure is read for an air temperature equal to the temperature of the thermostat; from this the extent of the decomposition of the acid can be determined.

EXPERIMENTAL RESULTS

The results obtained by this method are given in Tables 1 and 2. In order that the various acids may be compared, the measured excess pressure has been recalculated for 1 mole of acid.

The residual pressure in the case of oxalic acid was 306 mm Hg, and the percentage of acid decomposed was: a) (calculated from residual pressure) 31.2; b) (calculated from titration results) 31.1.

In the case of malonic acid the residual pressure was 205 mm Hg, whence we obtain 21.6% decomposed acid (by titration, 21.2%).

It will be seen from the results in Tables 1 and 2 and in Figure 2 that with increase in the molecular weight of the acid the thermal stability increases. The first members of the homologous series are notable for their insignificant thermal stability and differ greatly in their behavior from the remaining dicarboxylic acids. It will be seen that, judging from the behavior of malonic, glutaric, and azelaic acids, acids containing an odd number of carbon atoms decompose more readily than the adjacent members, which have an even number of carbon atoms.

TABLE 1

Acid	Oxalic		Malonic	
Molecular Weight	90		104	
Amount taken, g	0.3808		0.4318	
Temperature, °C \ Pressure mm Hg	p	$\frac{p \cdot M}{m}$	p	$\frac{p \cdot M}{m}$
100	0-2	60	0-2	160
110	0-2	120	0-2	320
120	0-2	180	2	480
130	1	240	6	1 400
140	2	470	18	4 300
150	10	2 400	98	24 000
160	36	8 500	166	40 000
170	130	31 000	210	51 000
180	320	76 000		

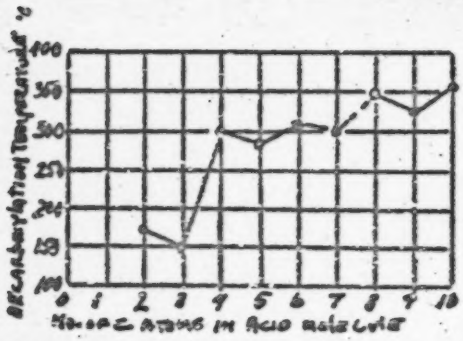


Fig. 3. Variation in decarboxylation temperature of dicarboxylic acids with the number of carbon atoms in the acid molecule.

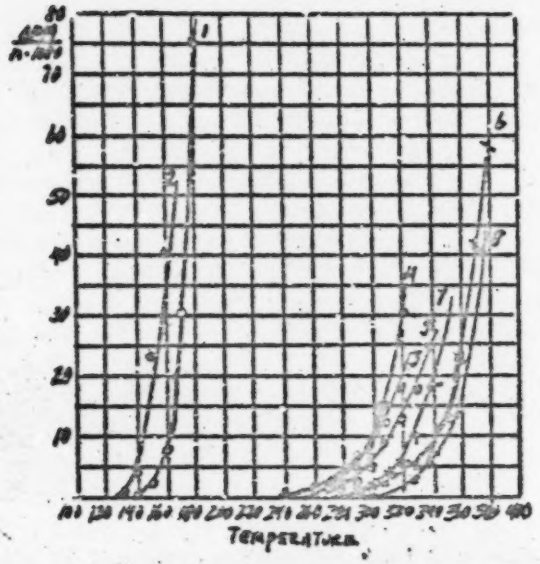


Fig. 2. Decomposition of dicarboxylic acids: 1) oxalic; 2) malonic; 3) succinic; 4) glutaric; 5) adipic; 6) suberic; 7) azelaic; 8) sebacic.

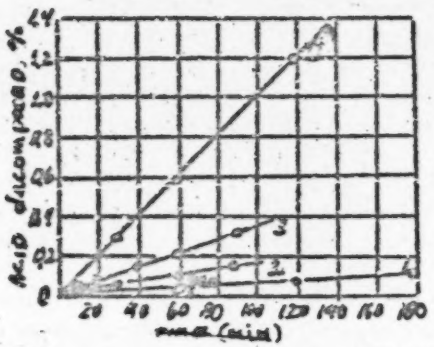


Fig. 4. Dependence of rate of decomposition of adipic acid on temperature. 1) 250°; 2) 260°; 3) 270° and 4) 280°.

Each acid decomposes most vigorously on reaching a definite temperature, which may be termed the decarboxylation temperature.

Decarboxylation temperatures of the acids investigated are given in Table 3.

The variation in the decarboxylation temperature with increase in the chain length of the dicarboxylic acid is shown in Figure 3. The experiments carried out at constant temperature permit a more exact estimate of the temperature below which no appreciable decomposition is observed. It was established that in the case of adipic acid there was no appreciable decomposition at below 240° (Table 4).

The results obtained on the decomposition of adipic acid at constant temperatures enable us to make an estimate of the variation of reaction rate with temperature. Since the slope of the straight line (Figure 4) is determined by the rate of reaction, the variation of tgα with temperature gives the variation of reaction rate with temperature:

1) 250° $tg\alpha_1 = 0.044$
2) 260° $tg\alpha_2 = 0.13$
3) 270° $tg\alpha_3 = 0.356$
4) 280° $tg\alpha_4 = 1.0$

TABLE 2

Acid	Succinic		Glutaric		Adipic		Suberic		Azelaic		Sebacic	
Molecular Wt.	118		132		146		174		188		202	
Amount taken, g	0.4659		0.1580		0.3850		0.2932		0.3148		0.3234	
Temperature °C \ Pressure in mm Hg	p	$\frac{p \cdot M}{m}$	p	$\frac{p \cdot M}{m}$	p	$\frac{p \cdot M}{m}$	p	$\frac{p \cdot M}{m}$	p	$\frac{p \cdot M}{m}$	p	$\frac{p \cdot M}{m}$
200	1-2	250	–	–	–	–	–	–	–	–	–	–
210	0-2	380	–	–	–	–	–	–	–	–	–	–
220	2	400	–	–	0-2	150	–	–	–	–	–	–
230	3	530	0-2	420	0-2	300	–	–	–	–	–	–
240	3-4	880	0-2	840	0-2	450	–	–	–	–	–	–
250	6-8	1 800	2	1 700	2	600	0-2	200	–	–	–	–
260	10	2 500	2-3	2 100	3	780	0-2	600	–	–	–	–
270	12	3 000	3-4	2 900	4	1 100	0-2	900	0-2	400	–	–
280	16	4 100	4	3 300	6	2 300	2	1 200	0-2	810	0-2	410
290	19	4 900	7	5 800	9	3 800	3	1 800	2	1200	0-2	820
300	28	7 100	13	11 000	15	5 700	4	2 400	4	2 500	2	1 200
310	50	13 000	20	17 000	25	9 500	5	3 000	8	4 900	2	1 200
320	72	18 000	38	32 000	56	14 000	7	4 100	11	6 800	3	1 900
330	–	–	–	–	48	18 000	9	5 300	17	10 000	6	3 700
340	–	–	–	–	66	25 000	12	7 100	32	15 000	10	6 000
350	–	–	–	–	–	–	19	11 000	50	31 000	22	14 000
360	–	–	–	–	–	–	40	29 000	–	–	45	28 000
370	–	–	–	–	–	–	72	43 000	–	–	63	42 000
380	–	–	–	–	–	–	100	59 000	–	–	–	–

The temperature coefficient of the reaction rate is given by a ratio of tangents

$$\frac{tg\alpha_2}{tg\alpha_1} = \frac{0.13}{0.044} = 2.95;$$

$$\frac{tg\alpha_3}{tg\alpha_2} = \frac{0.356}{0.13} = 2.75;$$

$$\frac{tg\alpha_4}{tg\alpha_3} = \frac{1.0}{0.356} = 2.82.$$

The mean value of the coefficient is 2.84.

Oxalic acid behaves in a similar way. It was found that oxalic acid does not decompose appreciably below 110°. The results obtained in the study of the decomposition of the acids at constant temperatures enables us to calculate activation energies, reaction rate constants, and also the orders of the reactions.

TABLE 3

No.	Name of acid	Temp. °C
1	Oxalic	170
2	Malonic	150
3	Succinic	300
4	Glutaric	285
5	Adipic	310
6	Suberic	350
7	Azelaic	330
8	Sebacic	360

TABLE 4

Decomposition temp. 250°		Decomposition temp. 260°		Decomposition temp. 270°		Decomposition temp. 280°	
Duration of decomposition (min.)	% of decomposition	Duration of decomposition (min.)	% of decomposition	Duration of decomposition (min.)	% of decomposition	Duration of decomposition (min.)	% of decomposition
60	0.0272	15	0.0173	10	0.04	30	0.298
120	0.0546	30	0.042	20	0.08	60	0.62
180	0.082	60	0.085	40	0.13	120	1.14
–	–	90	0.129	60	0.20	–	–
–	–	–	–	90	0.31	–	–

The activation energy was calculated from the Van't Hoff-Arrhenius equation

$$\ln\frac{k_1}{k_2} = \frac{A}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

where the values of the tangents may be inserted in place of k_1 and k_2 (see

Table 6) The value of the constant calculated from the first-order equation

$$k = \frac{1}{t}\ln\frac{a}{a-k}$$

remains approximately constant, and the decomposition of adipic acid may be regarded as a first-order reaction. The values of k are given in Table 5.

DISCUSSION OF RESULTS

The results we have obtained show that dicarboxylic acids very readily decompose at elevated temperatures, giving carbon dioxide and the corresponding monocarboxylic acid according to the equation:

$$HOOC(CH_2)_nCOOH \rightarrow CH_3(CH_2)_{n-1}COOH + CO_2$$

The monocarboxylic acids formed in the decomposition of oxalic and malonic acids were isolated by us and identified. Formic acid is formed from oxalic, acetic from malonic, etc. This decarboxylation reaction must play an important part in the processes of polycondensation between dicarboxylic acids and other bifunctional compounds. The results that follow from this may be of two kinds. In the first place, as a result of decarboxylation and conversion of dicarboxylic acids into monocarboxylic acids, there is a reduction in the total number of reactive groups, which must lead to a reduction in the molecular weight of the polycondensation products obtained owing to the disturbance in the molecular ratio of the initial substances. Presence of excess of one or other of the initial substances leads to a lowering of the molecular weight of the polycondensation product to an extent that is directly proportional to the excess; this has been shown by one of us on the basis of a large number of examples [15]. In the second place, the monocarboxylic acids formed "close" the end-groups and bring chain growth to a halt, thus lowering the molecular weight of the product formed. Finally, if the polycondensation reaction is proceeding at temperatures higher than the decarboxylation temperature, all possibility, even in principle, of obtaining a macromolecular polycondensation product disappears.

TABLE 5

Temp. of decomposition of acid (°C)	Duration of decomposition (hr)	% decomposition of acid	$k = \frac{1}{t} \ln \frac{a}{a-k} \cdot 10^{-2}$	Mean value of constant $\cdot 10^{-2}$
250	1.0	0.0272	0.0278	
250	2.0	0.0546	0.0276	0.0276
250	3.0	0.082	0.0275	
260	0.25	0.0178	0.0828	
260	0.5	0.042	0.0856	
260	1.0	0.085	0.0851	
260	1.5	0.129	0.0858	0.0848
260	0.167	0.04	0.241	
260	0.333	0.08	0.241	
260	0.666	0.13	0.1935	
270	1.0	0.20	0.203	0.2277
270	1.5	0.31	0.260	
280	0.5	0.298	0.581	
280	1.0	0.62	0.621	0.5916
280	1.5	1.14	0.573	

TABLE 6

	Temp. intervals (°C)			Mean value
	250-260	260-270	270-280	
1 $\frac{k_{t+10}}{kt}$	3.072	2.685	2.598	2.785
2 $\frac{tg\alpha_{t+10}}{tg\alpha}$	2.95	2.75	2.82	2.84
3 Activation energy calculated from tangent ratio	59 778	58 208	61 600	59 860
4 Activation energy calculated from constants	62 089	56 729	56 293	58 570

It now becomes clear why acids such as oxalic and malonic do not give macromolecular polyesters and polyamides as the result of polycondensation reactions with glycols and diamines, for they readily decompose at fairly low temperatures.

SUMMARY

1. A method has been developed for the determination of the thermal stability and decomposition kinetics for organic carboxylic acids.

2. The decarboxylation temperatures have been determined for oxalic, malonic, succinic, glutaric, adipic, suberic, azelaic, and sebacic acids.

3. It has been found that dicarboxylic acids having an odd number of carbon atoms decompose at lower temperatures than acids having an even number of carbon atoms.

4. It has been shown that the thermal stability of the acid increases as we proceed from the lower to the higher members of the homologous series of dicarboxylic acids.

5. It has been shown that decarboxylation of dicarboxylic acids must play a considerable inhibiting role in the course of the polycondensation of these acids with bifunctional substances.

6. On the basis of the results on the thermal decomposition of adipic acid, calculations have been made of reaction order and activation energy.

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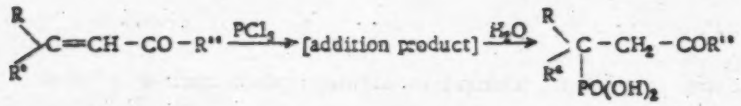
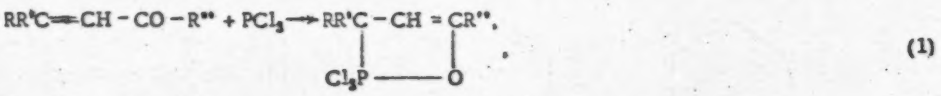
THE REACTION OF PHOSPHORUS TRICHLORIDE WITH UNSATURATED CYCLIC KETONES

M.I.Kabachnik and T.Ya.Medved

α,β-Unsaturated ketones, as is well known, react at room temperature with phosphorus trichloride in a medium of acetic anhydride or of glacial acetic acid with formation of addition products, which are converted by hydrolysis into γ-oxoalkylphosphonic acids [1]:

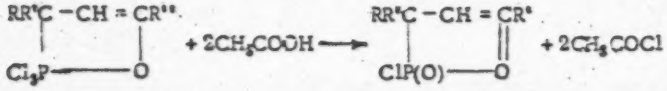


Conant and Cook suggested [2] that the mechanism of the reaction involves 1,4-addition of phosphorus trichloride:



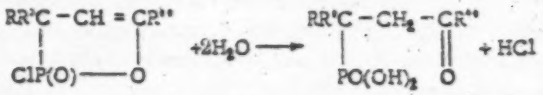
(1)

acetolysis of this intermediate product giving the acid chloride (or anhydride) of a "lactono acid":



(2)

and finally hydrolysis of this acid chloride (or anhydride):

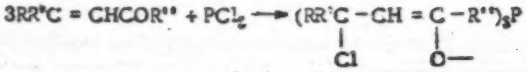


(3)

This scheme is reproduced in many reviews and books concerning the chemistry of organophosphorus compounds [3]. Evidence in its favor is to be found in the isolation of several cyclic acid chlorides, formed in the second stage, in a pure form [4].

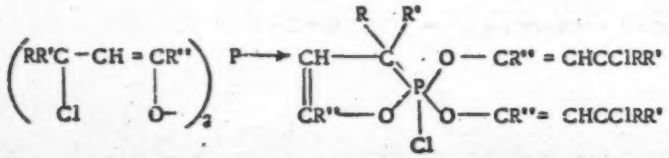
It was suggested by one of us [1] that Conant's scheme is incorrect. This supposition was based on the improbability of such direct alkylation of the phosphorus of phosphorous trichloride, which is so difficult to alkylate, even with alkyl halides.

An alternative to Conant's scheme was suggested in which there occurs 1,4-addition of Cl and the PCl_2 group with formation of a γ-halo unsaturated ester of phosphorous acid:



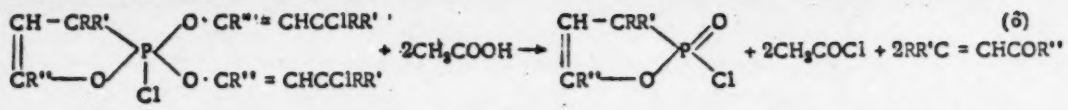
(4)

which undergoes the first stage of the A.E.Arbuzov rearrangement:



(5)

This intermediate product then undergoes acetolysis:

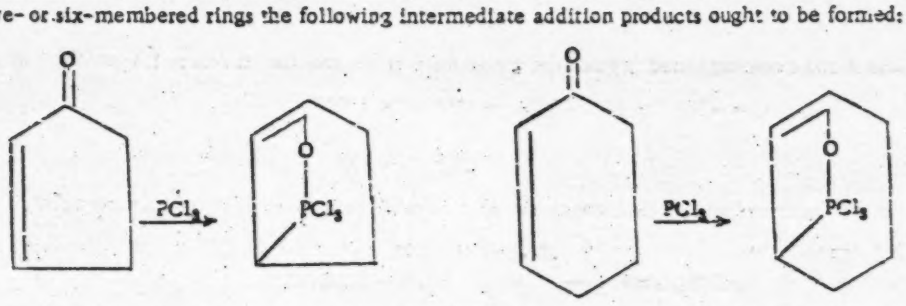


(6)

with formation of a cyclic acid chloride, identical with that assumed in Conant's scheme. The further hydrolysis of the acid chloride leads to a γ-oxoalkylphosphonic acid, in accordance with Equation 3. The regenerated unsaturated ketone again reacts with PCl_3, etc.

We pointed out also that formation of the cyclic acid chloride is not bound to be a stage in the course of this reaction, for the alkylation of a phosphorous ester [5] is not bound to proceed intramolecularly, but may proceed also intermolecularly. Similar phenomena were observed by Kabachnik and Rossiyskaya in a study of the reaction between phosphorus trichloride and ethylene oxide [5], and by Kabachnik and Shepeleva in the reaction between saturated aldehydes and phosphorus trichloride [6]. The scheme we have proposed is in accord with the results of the investigations cited. Nevertheless, it would be impossible to make a choice between the suggested schemes on the basis of the experimental material available in the literature.

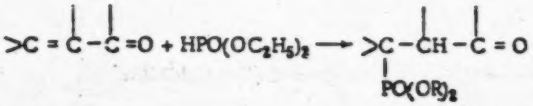
We decided to verify Conant's scheme in the following manner. If the reaction between unsaturated ketones and phosphorus trichloride proceeds by Conant's scheme, then when the reaction occurs with unsaturated cyclic ketones having five- or six-membered rings the following intermediate addition products ought to be formed:



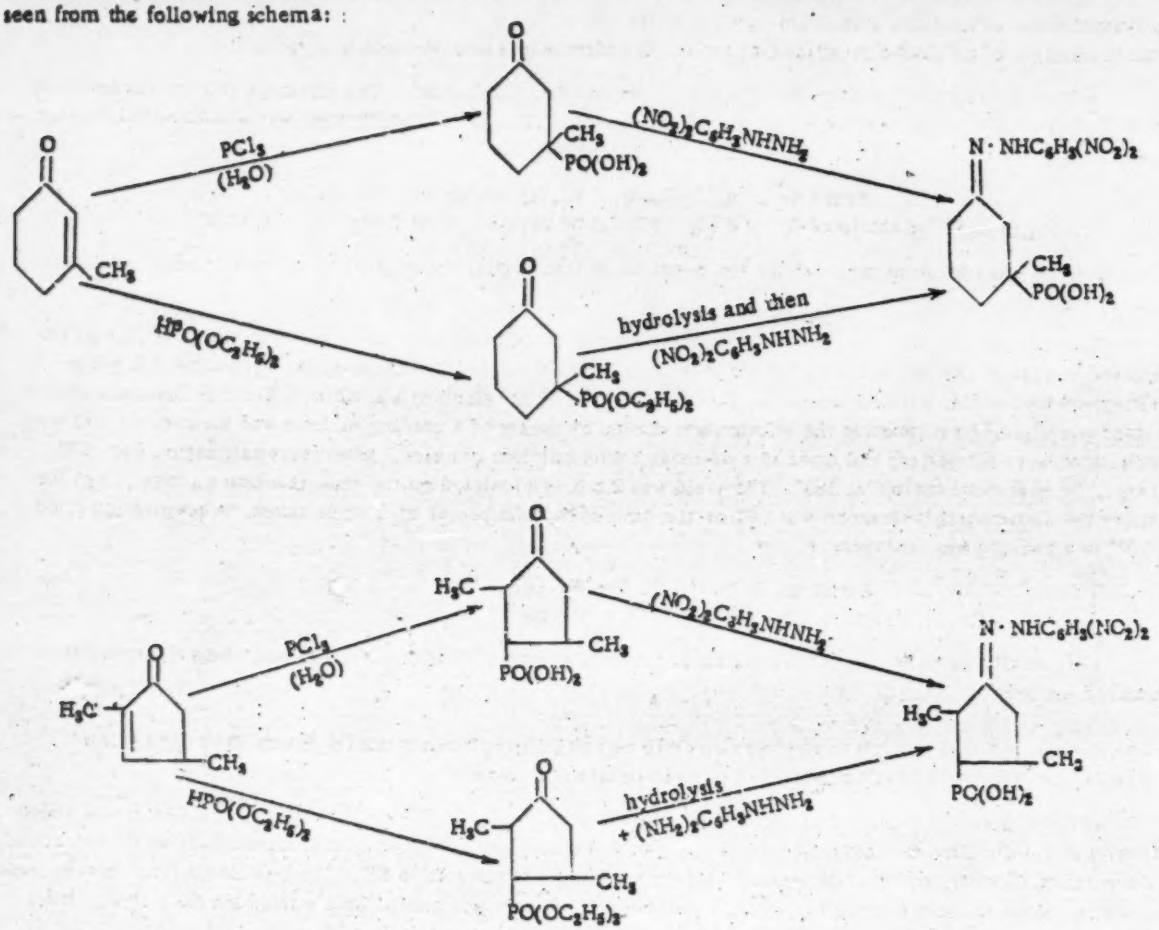
However, molecules of such a structure cannot be formed, for they are bound to be extremely strained; they will contain a multiple bond at the carbon atom that is at the base of the bridge of the bicyclic system. Hence, according to Conant's scheme, unsaturated cyclic ketones cannot add phosphorus trichloride, and therefore the reaction cannot go at all. If, however, phosphorus trichloride does add to unsaturated cyclic ketones with formation after hydrolysis of cyclic γ-oxo acids, then it is clear that the addition reaction proceeds by some other scheme, distinct from that of Conant—probably in accordance with ours.

We have carried out the reactions between phosphorus trichloride and two α,β-unsaturated cyclic ketones: 3-methyl-2-cyclohexen-1-one [8] and 2,4-dimethyl-2-cyclopenten-1-one [7]. Phosphorus trichloride readily adds to each of these ketones in acetic acid solution, and the reaction products yield on hydrolysis the corresponding oxocycloalkylphosphonic acids, which we did not succeed in preparing in crystalline form, since they form syrups; they yield, however, 2,4-dinitrophenylhydrazones and p-toluidine salts that crystallize well. From 3-methyl-2-cyclohexen-1-one we obtained the 2,4-dinitrophenylhydrazone of the oxophosphonic acid, m.p. 197°, and from 2,4-dimethyl-2-cyclopenten-1-one we obtained a 2,4-dinitrophenylhydrazone, m.p. 188°, and a p-toluidine salt, m.p. 153-154°.

In order to prove the structure of the keto acids obtained, and of their derivatives, we made use of the recently described reaction of Pudovik and B.A.Arbuzov [9], in which diethylphosphorous acid (diethyl phosphonate) is added to α,β-unsaturated ketones in presence of metallic sodium. This reaction resembles the well known addition reaction of malonic ester at the double bond of an α,β-unsaturated ketone, and there is no doubt that the phosphonic residue adds at the third carbon atom:



On the addition of diethylphosphorous acid to our unsaturated cyclic ketones the formation must occur of the same cyclic γ-oxophosphonic acids must occur as are obtained by the addition of phosphorus trichloride, as will be seen from the following schema:



Diethylphosphorous acid added readily to each of the unsaturated cyclic ketones with formation of esters of cyclic γ-oxophosphonic acids, which were readily distilled under reduced pressure and were therefore readily purified. When these esters were hydrolyzed by means of hydrochloric acid (1:1), siruplike oxophosphonic acids were formed which, like those obtained by the first method, gave well-crystallizing 2,4-dinitrophenylhydrazones of m.p. 195 and 186° respectively; mixed tests of the hydrazones obtained by the two methods showed no depression in the m.p.; their identity was confirmed also by examination in the polarization microscope: the crystals obtained from the ketone having a six-membered ring (m.p. 195° and 197°) are rhombic in form with an apex angle of 78° and with direct extinction along the diagonal of the rhombus; the crystals obtained from the ketone having a five-membered ring (m.p. 188° and 186°) have the form of very small, fine needles having direct extinction along the axis and perpendicular to the axis.

Thus, it has been proved that addition of phosphorus trichloride to α,β-unsaturated cyclic ketones leads to the corresponding γ-oxophosphonic acids and cannot therefore proceed according to Conant's schema.

EXPERIMENTAL

Preparation of 2,5-Dimethyl-3-exocyclopentylphosphonic Acid from 2,4-Dimethyl-2-cyclopenten-1-one and Phosphorus Trichloride

Phosphorus trichloride (6.9 g) was added gradually to a mixture of 2,4-dimethyl-2-cyclopenten-1-one (b.p. 82-84° at 47 mm; n_D^{20} 1.4647), (5.5 g) and glacial acetic acid (6 g). The reaction is carried out with cooling; the temperature of the reaction mixture did not exceed + 15° – + 20°. The reaction mixture was left overnight and was then carefully poured into ice water. The water and acetic acid were driven off under reduced pressure, and the

residue, a thick dark-colored mass, was dried in a vacuum desiccator over calcium chloride. A syrup (10 g), readily soluble in alcohol but of poor solubility in ether, was obtained. It was not found possible to purify the substance by recrystallization or reprecipitation. On addition to the alcoholic solution of the substance of a solution of p-toluidine in ether, or of an alcoholic solution of aniline, a voluminous white precipitate is formed.

p-Toluidine Salt of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid. The substance (0.6 g) was dissolved in alcohol, and an ethereal solution of p-toluidine was added. The precipitate formed was washed with ether and dried in a desiccator (0.74 g, m.p. 153-154°).

	Found %:	N 4.27;	4.35;	C 56.74;	56.76;	H 7.55;	7.72;	P 10.64; 10.06
$C_{14}H_{22}O_4NP$.	Calculated %:	N 4.67;		C 56.20;		H 7.36;		P 10.35

When attempts were made to recrystallize the p-toluidine salt, partial decomposition of the salt occurred and the m.p. was reduced.

2,4-Dinitrophenylhydrazone of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid. The substance (2.0 g) was dissolved in ethanol (80 ml) and a freshly prepared alcoholic solution of 2,4-dinitrophenylhydrazine (1.6 g 2,4-dinitrophenylhydrazine, 8 ml sulfuric acid, 12 ml water, and 40 ml alcohol) was added. The mixture was allowed to stand overnight. Next morning the solution was cooled by means of a cooling mixture and the crystals that were precipitated were filtered off and dried in a desiccator over calcium chloride. After recrystallization from 96% ethanol, the hydrazone melted at 188°. The yield was 2.5 g. Calculated on the total reaction mixture (10 g) the yield of the dinitrophenylhydrazone was 66% on the basis of the phosphorus trichloride taken. A preparation dried at 100° in a vacuum was analyzed:

	Found %:	N 14.70;	14.90;	P 8.60;	8.80
$C_{13}H_{17}PN_4O_7$.	Calculated %:	N 15.0;		P 8.33	

Very small fine needles; in the polarization microscope they show direct extinction along the axis and normal to the axis.

Preparation of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid from Diethylphosphorous Acid and 2,4-Dimethyl-2-cyclopenten-1-one

a) Ethyl Ester of 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid. Diethylphosphorous acid (14 g) was added gradually to 2,4-dimethyl-2-cyclopenten-1-one (11 g). A few drops of a solution of sodium ethoxide were then added to the reaction mixture, and the temperature of the reaction mixture rose to 55°. The reaction mixture was cooled with water. When the self-heating had ceased, the reaction mixture was heated on a water bath for 3 hours. It was then vacuum-distilled. As a result of three distillations there was separated a fraction having a b.p. of 119-120° at 3 mm (5.1 g, 20% of theoretical); n_D^{20} 1.4553; d_4^{20} 1.1022; calculated MR_D 61.67; found MR_D 61.10.

	Found %:	C 53.19;	53.32;	H 8.31;	8.43;	P 12.12;	12.10.
$C_{11}H_{21}O_4P$.	Calculated %:	C 53.23;		H 8.47;		P 12.50	

b) 2,5-Dimethyl-3-oxocyclopentylphosphonic Acid. The ethyl ether of dimethyloxocyclopentylphosphonic acid (2.5 g) and hydrochloric acid (1:1) (75 ml) were boiled under reflux for 15 hours. The solution was then evaporated down on the water-bath, and the residue, a dark-yellow viscous liquid, was dried in a vacuum desiccator over calcium chloride for several days until constant weight was attained. A syrup was obtained.

2,4-Dinitrophenylhydrazone. This was obtained as for the previous hydrazone from 1 g of the syrup and 0.8 g of 2,4-dinitrophenylhydrazine. After two crystallizations from ethanol, bright-yellow crystals (0.9 g, m.p. 186°) were obtained. In admixture with the 2,4-dinitrophenylhydrazone of 2,5-dimethyl-3-oxocyclopentylphosphonic acid obtained by the PCl_3 reaction, it melted at 188°. On examination of the two preparations under the polarization microscope, they appeared to be completely identical.

Preparation of 1-Methyl-3-oxocyclohexylphosphonic Acid from 3-Methyl-2-cyclohexen-1-one and Phosphorus Trichloride.

Freshly distilled phosphorus trichloride (6.9 g) was added to 3-methyl-2-cyclohexen-1-one (b.p. 201-203°; n_D^{20} 1.4926) (5.5 g); the mixture became yellow and its temperature rose to 25°. After 1½ hours, glacial acetic acid (9 g) was added to the mixture; the temperature again rose to 23-25°. The mixture was allowed to stand until the next day, when it was carefully poured into ice water. The water and acetic acid were driven off under reduced pressure, and the residue, a thick brown liquid, was dried in a desiccator over calcium chloride. The syrup did not

crystallize after long standing in the desiccator. Yield 9.8 g; it was of good solubility in water and in alcohol, poorly soluble in ether, and insoluble in chloroform. The acid obtained was impure and contained phosphoric acid contamination. The p-toluidine salt has m.p. 147°, the aniline salt m.p. 152°.

2,4-Dinitrophenylhydrazone. The substance (5 g) was dissolved in ethanol (200 ml), and a freshly prepared alcoholic solution of 2,4-dinitrophenylhydrazine (4 g 2,4-dinitrophenylhydrazine, 20 ml sulfuric acid, 30 ml water, and 100 ml ethanol) was added. The mixture was allowed to stand overnight. On the next morning the solution was cooled by means of a cooling mixture, and the crystals that were precipitated were filtered off and dried in a desiccator over calcium chloride. M.p. after recrystallization from ethanol: 197°. The substance crystallizes with one molecule of alcohol; 6.2 g was obtained. The 2,4-dinitrophenylhydrazone forms rhombic crystals having an apex angle of 78°. Under crossed nicols there is direct extinction along the diagonal of the rhombus.

Found %: C 42.55; 42.90; H 5.67; 5.67; N 13.85; 13.90;
P 7.14; 7.15; C_2H_5OH (in a vacuum at 100°) 10.5%.

$C_{13}H_{17}PN_4O_7C_2H_5OH$. Calculated %: C 43.06, H 5.50; N 13.40;
P 7.42, C_2H_5OH 11.0

After being vacuum-dried, the substance melts at 195°.

Found %: P 8.70.

$C_{12}H_{17}PN_4O_7$. Calculated %: P 8.30.

Preparation of 1-Methyl-3-oxocyclohexylphosphonic Acid from Diethylphosphorous Acid and 3-Methyl-2-cyclohexen-1-one

a) Ethyl Ester of 1-Methyl-3-oxocyclohexylphosphonic Acid. Diethylphosphorous acid (14 g) was added to methylcyclohexenone (b.p. 86-89° at 12 mm; n_D^{20} 1.4927) (11 g), and a few drops of a solution of sodium ethoxide were then added to the reaction mixture; the temperature of the reaction mixture rose to 72°. The reaction mixture was heated further for 3 hours on a boiling water-bath, and was then vacuum-distilled. After redistilling, a substance was isolated of b.p. 120-124° at 2 mm (10 g; 40%), colorless liquid; d_4^{20} 1.1188; n_D^{20} 1.4638; found MR_D 61.14, calculated MR_D 61.67.

Found %: C 53.40; 53.30; H 8.39; 8.39; P 12.40; 12.10

$C_{11}H_{21}O_4P$. Calculated %: C 53.23; H 8.47; P 12.50

b) Methyl Ester of 1-Methyl-3-oxocyclohexylphosphonic Acid. Dimethylphosphorous acid (b.p. 72-73° at 10 mm; n_D^{20} 1.4923) (11 g) was added to methylcyclohexenone (b.p. 33° at 3 mm; n_D^{20} 1.3991) (11 g), and a few drops of sodium methoxide solution were then added to the reaction mixture, when the temperature rose to 55°. The reaction mixture was heated further for 3 hours on the water-bath, and on the next day it was vacuum-distilled. After two distillations the fraction of b.p. 127-129° at 2mm was separated, and this crystallized out. The substance obtained melted at 48°.

Found %: C 48.70; 48.70; H 7.40; 7.60; P 13.90; 14.00

$C_9H_{17}PO_4$. Calculated %: C 49.10; H 7.70; P 14.10

c) 1-Methyl-3-oxocyclohexylphosphonic Acid. The ethyl ester of methyloxocyclohexylphosphonic acid (b.p. 124-127° at 2 mm; n_D^{20} 1.4642) (2.5 g) and hydrochloric acid (30 ml, 1:1) were heated in a sealed tube at 130-135° for 2 hours. The contents of the tube were then evaporated down on the water-bath to constant weight. The residual thick dark-yellow liquid was dried in a vacuum desiccator over phosphorus pentoxide to constant weight (several days). The result was a non-crystallizing syrup.

2,4-Dinitrophenylhydrazone. The substance (1.9 g) was dissolved in alcohol (75 ml), and a freshly prepared solution of 2,4-dinitrophenylhydrazine (1.5 g 2,4-dinitrophenylhydrazine, 7.5 ml sulfuric acid, 11.2 ml water, and 37 ml alcohol) was added. The mixture was left overnight, and the crystals that separated were filtered off. After recrystallization from ethanol, bright-yellow glistening crystals were obtained (1 g, m.p. 195°). M.p. in admixture with the 2,4-dinitrophenylhydrazone of m.p. 197° obtained from methylcyclohexenone and phosphorus trichloride was 197°. The two preparations appeared to be identical under the polarization microscope.

SUMMARY

1. Phosphorus trichloride adds to α,β-unsaturated cyclic ketones with formation after hydrolysis of cyclic γ-oxophosphonic acids.

2. Cyclic γ-oxophosphonic acids of identical structure are obtained by the addition of diethylphosphorous acid to α,β-unsaturated cyclic ketones and the subsequent hydrolysis of the esters formed.

3. The fact that cyclic γ-oxophosphonic acids are formed from α,β-unsaturated cyclic ketones disproves Conant's hypothesis concerning the mechanism of the addition of phosphorus trichloride to α,β-unsaturated ketones.

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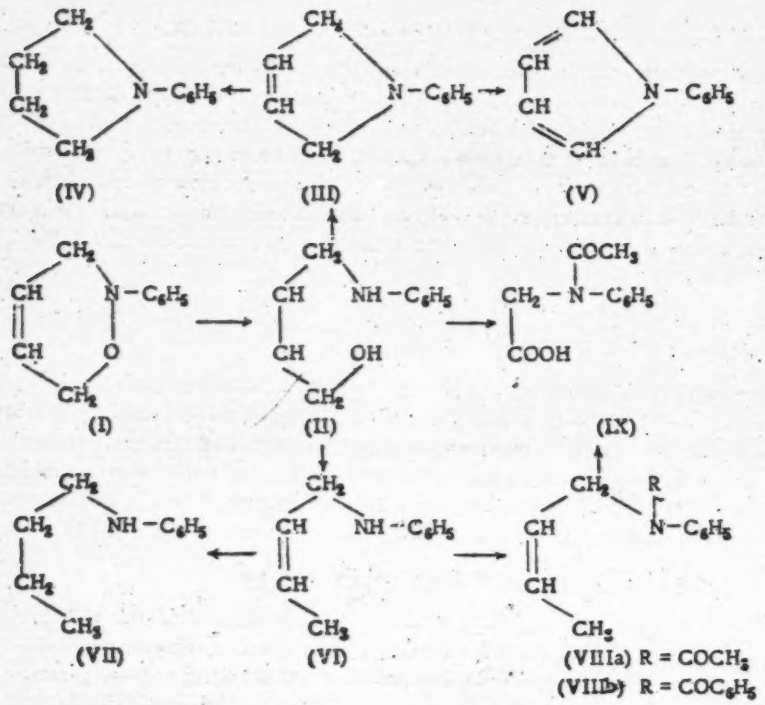
THE REACTIONS OF DIENIC HYDROCARBONS WITH NITROSO COMPOUNDS. ADDITION OF 1,3-BUTADIENE TO NITROSOBENZENE. COMMUNICATION 2.

Yu. A. Arbuzov

It was shown in the previous communication [1] that 1,3-butadiene adds on to nitrosobenzene in accordance with the diene synthesis with formation of 3,6-dihydro-2-phenyl-1,2,2H-oxazine. In this paper, results of experiments on the reduction of this phenyldihydroxazine are given.

It was previously found that reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I) with zinc dust and acetic acid leads to formation of 4-phenylamino-2-buten-1-ol (II). If, after reducing (I) in this way, the reaction mixture is heated for several hours, then the main reaction product is a crystalline tertiary amine, m.p. 101-102°. Elementary analysis showed that the amine had the composition $C_{10}H_{11}N$. The same amine was obtained by heating 4-phenylamino-2-buten-1-ol (II) with a solution of zinc chloride in acetic or hydrochloric acid, or with a mixture containing acetic, phosphoric, and hydrobromic acids and a small amount of phosphoric anhydride.



It was considered that the tertiary amine, m.p. 101-102°, was 1-phenyl-3-pyrroline (III), formed by the splitting of water from 4-phenylamino-2-buten-1-ol (II). This supposition has been confirmed. Catalytic reduction of the amine gives 1-phenylpyrrolidine (IV), which was identified in the form of its picrate. Oxidation of the amine with potassium permanganate or ferric chloride gives 1-phenylpyrrole (V).

Thus, by means of the reactions indicated we have succeeded in converting a dihydro-o-oxazine ring into a pyrroline ring. (See above).

Different results were obtained when the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I) was carried out with sodium and methyl, ethyl, or butyl alcohol. In all these experiments, the main reaction product was a secondary amine (b.p. 89-90° at 3 mm) of composition $C_{10}H_{13}N$. The amine was characterized by means of its acetyl

derivative (b.p. 108-109° at 2 mm) and its benzoyl derivative (m.p. 90-91°).

It was considered that the secondary amine of b.p. 89-90° at 3 mm was N-2-butenylaniline (VI), formed from (I) via (II) by further reduction. This supposition was confirmed. Catalytic reduction of the amine gives N-butylaniline (VII), identified as its benzoyl derivative. On oxidation of the acetyl derivative of the amine (VIIIa) with potassium permanganate in acetone, N-acetyl-N-phenylglycine (IX) is formed. Hydrolysis of the acetyl or benzoyl derivative of the amine (VIIIa or VIIIb) with conc. hydrochloric acid yields a crystalline hydroxy amine (m.p. 60.5-61.5°) of composition $C_{10}H_{15}ON$. This hydroxy amine, which is the product formed by addition of the elements of water at the double bond of N-2-butenylaniline (VI), has been prepared previously by Yu. A. Arbuzov and Garburg [2] by hydrolysis with conc. hydrochloric acid of the benzoyl derivative of N-2-butenylaniline, prepared by the reduction of 1-phenylpyrrole with zinc dust and acid.

When 4-phenylamino-2-buten-1-ol (II) is reduced with sodium and ethanol under the same conditions as those employed for the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I), N-2-butenylaniline (VI) is formed. In a further experiment, 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I) was reduced by sodium and ethanol to 4-phenylamino-2-buten-1-ol (II), the amount of sodium taken being one-quarter of the amount used in the previous experiments. N-2-Butenylaniline (VI) and 4-phenylamino-2-buten-1-ol (II) were isolated from the products of reaction. The latter could not be separated in the pure state and was converted, for identification, into its dibenzoyl derivative, which melted at 88-89°. The m.p. of a mixture with the pure dibenzoyl derivative of 4-phenylamino-2-buten-1-ol (m.p. 90-91°) was 88-89°. From the above results it follows that, on reduction with sodium and alcohol, 3,6-dihydro-2-phenyl-1,2,2H-oxazine (I) gives 4-phenylamino-2-buten-1-ol (II), which is then reduced further to N-2-butenylaniline (VI).

EXPERIMENTAL

Conversion of 3,6-Dihydro-2-phenyl-1,2,2H-oxazine into 1-Phenyl-3-pyrroline

Expt. 1. Zinc dust (25 g) was introduced into a 250-ml round-bottomed flask containing 3,6-dihydro-2-phenyl-1,2,2H-oxazine (8.06 g; 0.05 mole) dissolved in glacial acetic acid (90 ml). The flask was stoppered and then shaken vigorously for 15 min. The reaction mixture became very hot. The flask was then fitted with a reflux condenser and heated on a water bath for 7 hours. The reaction mixture was cooled, diluted with water (250 ml), and made alkaline with potassium carbonate. The mixture was then steam-distilled. An almost colorless crystalline substance came over in the distillate, and this was filtered off and dried in a desiccator over sulfuric acid. 1-Phenyl-3-pyrroline (3.3 g; 45%), m.p. 95-98°, was obtained. M.p. after two recrystallizations from methanol: 101-102°. Colorless glistening plates.

	Found %:	C 82.69;	82.71;	H 7.58;	7.55;	N 9.69;	9.56.
$C_{10}H_{11}N$.	Calculated %:	C 82.71;		H 7.64;		N 9.65	

Expt. 2. Zinc dust (25 g) was introduced into a 250-ml round-bottomed flask fitted with a reflux condenser with a wide inner tube and containing a solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (16.1g 0.1 mole) in glacial acetic acid (50 ml). The flask was shaken, and the reaction mixture grew hot and finally boiled vigorously for several minutes. The mixture was then boiled for 4 hours. It was cooled, diluted with 100 ml of water, and rendered alkaline with a 40% solution of caustic soda. The 1-phenyl-3-pyrroline was steam-distilled off, filtered off, and dried (11.2 g; 77% of theoretical. M.p. 94.5-98°). M.p. after two recrystallizations from methanol: 101-102°.

Conversion of 4-Phenylamino-2-buten-1-ol into 1-Phenyl-3-pyrroline

Expt. 1. 4-Phenylamino-2-buten-1-ol (16.3 g, 0.1 mole) and a solution of anhydrous zinc chloride (10 g) in glacial acetic acid (50 ml) were introduced into a 100-ml round-bottomed flask fitted with a reflux condenser. The mixture was boiled for 4 hours. It was then cooled, and additions were made of 100 ml water and 100 g caustic soda. The 1-phenyl-3-pyrroline was steam-distilled off, filtered off, and dried (10.6 g; 73% of theoretical). M.p. after two recrystallizations from methanol: 100.5-101.5°.

Expt. 2. 4-Phenylamino-2-buten-1-ol (32.6 g, 0.2 mole) and 40 g of zinc chloride solution in conc. HCl (160 ml) were introduced into a 250-ml round-bottomed flask fitted with a reflux condenser. The mixture was boiled for 4 hours and then cooled. A 40% solution of caustic soda was added until the reaction was alkaline, and the 1-phenyl-3-pyrroline was steam-distilled off. The yield was 21.2 g (73% of theoretical). M.p. after recrystallization from methanol was 100-101°.

Expt. 3. 4-Phenylamino-2-buten-1-ol (32.6 g, 0.2 mole), 100 ml of glacial acetic acid, and 20 ml of 85% phosphoric acid were introduced into a 250-ml round-bottomed flask fitted with a reflux condenser. The mixture

was boiled for 5 hours, cooled, and rendered alkaline with a 40% solution of caustic soda. The 1-phenyl-3-pyrroline was steam-distilled off (15.6 g, 54% of theoretical). M.p. after recrystallization from methanol was 100-101°.

Expt. 4. 4-Phenylamino-2-buten-1-ol (16.3 g, 0.1 mole) and 50 ml of 40% hydrobromic acid were introduced into a 100-ml flask fitted with a reflux condenser. The mixture was boiled for 4 hours, cooled, and rendered alkaline with 40% caustic soda solution. The 1-phenyl-3-pyrroline was steam-distilled off (12.0 g, 83% of theoretical).

Expt. 5. 4-Phenylamino-2-buten-1-ol (32.6 g, 0.2 mole) and 1 g of phosphoric anhydride were introduced into a 100-ml distillation flask fitted with thermometer and air condenser arranged for distillation. The flask was heated on a metal bath. At first a small amount of water came over, and then, at 245-250°, 1-phenyl-3-pyrroline came over. The yield after steam-distillation was 24.1 g (83% of theoretical). M.p. after recrystallization from methanol was 99.5-101°.

Catalytic Reduction of 1-Phenyl-3-pyrroline into 1-Phenylpyrrolidine

1-Phenyl-3-pyrroline (7.25 g, 0.05 mole) was dissolved in 120 ml cyclohexane and reduced in presence of platinized (10% Pt) charcoal (1 g) at room temperature and pressure. Reduction was complete in 4 hours. Volume of hydrogen absorbed: 1330 ml (0° at 760 mm). The catalyst was filtered off, the cyclohexane was driven off, and the residue was vacuum-distilled. The product was 1-phenylpyrrolidine (6.0 g, 82% of theoretical) with the following constants: b.p. 102-103° at 5 mm; d_4^{28} 1.0157; n_D^{28} 1.5827; found MR_D 48.42; calculated MR_D 46.52;) EMR_D 1.90. Calculated 82% of theoretical. It solidified to a crystalline mass on being cooled with tap water.

Data in the literature [3]: b.p. 124° at 14 mm; [4] b.p. 110-116° at 9 mm; d^{25} 1.026; n_D^{25} 1.5803; [5] b.p. 114° at 9 mm; d_4^{28} 1.0183; n_D^{28} 1.5853; [2] b.p. 129-130° at 16 mm; d_4^{28} 1.0145; n_D^{28} 1.5920.

	Found %:	C 81.68, 81.43;	H 8.67, 8.78;	N 9.53, 9.47
$C_{10}H_{13}N$.	Calculated %:	C 81.59	H 8.90	N 9.51

1-Phenylpyrrolidine Picrate. A warm ethereal solution of picric acid (2.3 g, 0.01 mole) was mixed with an ethereal solution of 1.5 g. (0.01 mole) of 1-phenylpyrrolidine. Next day the picrate was filtered off and washed with ether (3.6 g, m.p. 114-115°). M.p. after recrystallization from ethanol was 116-117°. Data in the literature: [3] m.p. 114°; [4] m.p. 115-116°;) [5] m.p. 116°; [2] m.p. 116-117°.

For comparison, 1-phenylpyrrolidine and its picrate were prepared. The phenylpyrrolidine was obtained as follows: 1,4-dibromobutane (108 g, 0.5 mole) and freshly distilled aniline (140 g, 1.5 mole) were introduced into a 500-ml round-bottomed flask fitted with a reflux condenser. The mixture was heated on a boiling water-bath for 4 hours and then cooled. A 40% solution of caustic soda was added until the precipitate had completely dissolved. The oil that formed was separated, washed with 10% caustic soda solution and with water, dried with fused caustic soda, and vacuum-fractionated. The product was 1-phenylpyrrolidine (62.5 g, 85% of theoretical) with the following constants: b.p. 103-103.5° at 5 mm; d_4^{26} 1.0162; n_D^{26} 1.5829; found MR_D 48.40; calculated MR_D 46.52; EMR_D 1.88.. The picrate obtained from this preparation had a m.p. of 116-117° after recrystallization from ethanol. In admixture with the picrate of 1-phenylpyrrolidine obtained from 1-phenyl-3-pyrroline, it melted at the same temperature.

Oxidation of 1-Phenyl-3-pyrroline to 1-Phenylpyrrole by means of Potassium Permanganate

A solution of potassium permanganate (4.7 g, 0.03 mole) in 300 ml dry acetone was added over 2.5 hours with continuous stirring to a solution of 1-phenyl-3-pyrroline (4.35 g, 0.03 mole) in 300 ml dry acetone. Next day the precipitate was filtered off and the acetone driven off. 50 ml hydrochloric acid (diluted 1:1) was added to the residue, and the mixture was steam-distilled. A colorless crystalline substance went over into the distillate; it was filtered off, washed with water, and dried over sulfuric acid in a desiccator. The product was 1-phenylpyrrole (1.50 g, 35% of theoretical), m.p. 59.5-60.5°. In admixture with 1-phenylpyrrole (m.p. 60-61°) prepared from aniline mucate it melted at 60-61°. Data in the literature: [6] m.p. 62°; [7] m.p. 61.5°; [8] m.p. 60-61°; [9] m.p. 61-62°; [10] m.p. 60-61; [11] m.p. 60-61°; [12] m.p. 58°; [2] m.p. 61-62°.

Oxidation of 1-Phenyl-3-pyrroline to 1-Phenylpyrrole by means of Ferric Chloride

A solution of ferric chloride hexahydrate (10.8 g, 0.04 mole) in 50 ml water was added with stirring to a solution of 1-phenyl-3-pyrroline (2.90 g, 0.02 mole) in 50 ml hydrochloric acid (diluted 1:1). After 1 hour, the 1-phenylpyrrole was steam-distilled off (1.40 g, 49% of theoretical; m.p. 58-59°). In admixture with 1-phenylpyrrole

(m.p. 60-61°) prepared from aniline mucate it melted at 60-61°.

Reduction of 3,6-Dihydro-2-phenyl-1,2,2H-oxazine to N-2-Butenylaniline by means of Sodium and Alcohol

Expt. 1. A solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (32.2 g, 0.2 mole) in 650 ml absolute ethanol was introduced into a 3-liter round-bottomed flask fitted with a wide branched adapter and with a reflux condenser having a wide inner tube. The solution was heated to boiling, and 50 g sodium (about 2.2 g-atom) was introduced in small portions over 10 minutes. Heating was continued until the sodium had completely dissolved. The reaction mixture was cooled, and hydrochloric acid (diluted 1:1) was added until the solution became acid to Congo red. The alcohol was steam-distilled off. Potassium carbonate was added to give an alkaline reaction, and the mixture was steam-distilled. A light-yellow oil came over in the distillate. The oil was separated, and the aqueous layer was extracted three times with ether (3·100 ml). The ether extract was united with the oil, and the solution was dried with anhydrous sodium sulfate. The ether was driven off, and the residue was fractionated. N-2-Butenylaniline (19.9 g, 68% of theoretical) was obtained; it had the following constants: b.p. 89-90° at 3 mm; d_4^{20} 0.9613; n_D^{20} 1.5587; found MR_D 49.42; calculated MR_D 47.91; EMR_D 1.51. It is a colorless, fairly mobile liquid that gradually yellows during storage.

Found %: C 81.42, 81.43; H 8.86, 8.84; N 9.66, 9.76
$C_{10}H_{13}N$. Calculated %: C 81.59; H 8.90; N 9.51.

Expt. 2. A solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (48.3 g, 0.3 mole) in 1 liter absolute butanol was introduced into a 3-liter round-bottomed flask connected through a branched adapter to a reflux condenser. The solution was heated to boiling, and 75 g sodium (about 3.3 g-atom) was introduced in small portions over 15 minutes. Heating was continued until the sodium had completely dissolved. Further treatment was carried out as in Expt. 1. N-2-Butenylaniline (28.5 g, 65% of theoretical was obtained, with the following constants: b.p. 93-94° at 4.5 mm; d_4^{20} 0.9609; n_D^{20} 1.5587; found MR_D 49.44; calculated MR_D 47.91; EMR_D 1.53.

Expt. 3. A solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (32.2 g, 0.2 mole) in 500 ml absolute ethanol was introduced into a 3-liter round-bottomed flask connected through a branched adapter to a reflux condenser. The solution was heated to boiling, and 50 g sodium (about 2.2 g-atom) was introduced in small portions over 10 minutes. Heating was continued until the sodium had completely dissolved. The further treatment was as in the preceding experiments. N-2-Butenylaniline (12.0 g, 41% of theoretical) was obtained, with the following constants: b.p. 89-90° at 3 mm; d_4^{20} 0.9620; n_D^{20} 1.5590; found MR_D 49.40;) calculated MR_D 47.91; EMR_D 1.49.

Reduction of 4-Phenylamino-2-buten-1-ol to N-2-Butenylaniline by means of Sodium and Alcohol.

A solution of 4-phenylamino-2-buten-1-ol (16.3 g, 0.1 mole) in 350 ml absolute ethanol was introduced into a 2-liter round-bottomed flask connected through a branched adapter to a reflux condenser. The solution was heated to boiling, and 25 g sodium (about 1.1 g-atom) was introduced in small portions over 8 minutes. Heating was continued until the sodium had completely dissolved. The mixture was then cooled and acidified with diluted HCl. The alcohol was steam-distilled off, and the residue was rendered alkaline with potassium carbonate. N-2-Butenylaniline was steam-distilled over (9.9 g, 67% of theoretical), with the following constants: b.p. 87-88° at 2 mm; d_4^{20} 0.9611; n_D^{20} 1.5586; found MR_D 49.42; calculated MR_D 47.91; EMR_D 1.51.

Reduction of 3,6-Dihydro-2-phenyl-1,2,2H-oxazine to 4-Phenylamino-2-buten-1-ol by means of Sodium and Alcohol

A solution of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (32.2 g, 0.2 mole) in 350 ml absolute ethanol was introduced into a 2-liter round-bottomed flask connected through a branched adapter to a reflux condenser. The solution was heated to boiling, and 12.5 g sodium (about 0.54 g-atom) was introduced in the form of small cubes over 15 minutes. Heating was continued until the sodium had completely dissolved. The mixture was then cooled and acidified with hydrochloric acid. The alcohol was steam-distilled off, and the residue was rendered alkaline with 40% aqueous caustic soda. N-2-Butenylaniline was steam-distilled over (6.3 g), with the following constants: b.p. 90-91° at 3 mm; d_4^{20} 0.9628; n_D^{20} 1.5594; found MR_D 49.39; calculated MR_D 47.91; EMR_D 1.48.

The mixture that remained after distilling off the N-2-butenylaniline in steam was cooled and extracted 5 times with benzene (5·100 ml). The benzene solution was washed with water, the benzene was driven off, and the residue was vacuum-fractionated. A fraction (12.3 g) was collected with the following constants: b.p. 148-152° at 2 mm; d_4^{20} 1.1193; n_D^{20} 1.5866.

Benzoylation of the Fraction having a B.P. of 149-152° at 2 mm

Some of the fraction (4.90 g) and 60 ml of 10% aqueous caustic soda were introduced into a flask, and 14.1 g of benzoyl chloride was added in 5 portions over 30 minutes with energetic shaking. The excess benzoyl chloride was hydrolyzed by warming. The product of benzoylation was filtered off, washed with water, and recrystallized from ethanol. The product was the dibenzoyl derivative of 4-phenylamino-2-buten-1-ol (9.0 g), m.p. 87-88.5°. M.p. after repeated recrystallization from ethanol was 88-89°.

Found %: N 3.82, 3.94
$C_{24}H_{21}O_3N$. Calculated %: N 3.77

In admixture with the dibenzoyl derivative of 4-phenylamino-2-buten-1-ol obtained by the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine with zinc and acetic acid (m.p. 90-91°) it melted at 88-89°.

Catalytic Reduction of N-2-Butenylaniline to N-Butylaniline

N-2-Butenylaniline (7.36 g, 0.05 mole) was dissolved in 70 ml cyclohexane and reduced in presence of platinized (10% Pt) charcoal (1 g) at room temperature and pressure. Reaction was complete in 60 minutes. Volume of hydrogen absorbed: 1500 ml (0°, 760 mm). The catalyst was filtered off, the cyclohexane was driven off, and the residue was fractionated. N-Butylaniline (6.0 g, 80% of theoretical) was obtained; it had the following constants: b.p. 97-98° at 5 mm; d_4^{20} 0.9338; n_D^{20} 1.5361; found MR_D 49.83; calculated MR_D 48.38; EMR_D 1.45rature: Data in the literature: [14]; b.p.118-120° at 12 mm:[15]: b.p. 118-120° at 14 mm; [16]: b.p. 115-120° at 15 mm; ; d_4^{20} 0.9358; n_D^{20} 1.5381; b.p. 112-114° at 9 mm; d_4^{20} 0.9362; n_D^{20} 1.5373.

Found %: C 80.45, 80.69; H 10.05, 10.04; N 9.33, 9.10
$C_{16}H_{15}N$. Calculated %: C 80.50; H 10.12; N 9.38

Benzoylation of N-Butylaniline

N-Butylaniline (3.0 g, 0.02 mole) and 20 ml of 10% aqueous caustic soda were introduced into a flask, and 4.2 g (0.03 mole) benzoyl chloride was added in 3 portions over 15 minutes. After each addition of benzoyl chloride, the flask was closed by means of a stopper and shaken vigorously. Excess benzoyl chloride was hydrolyzed by warming on the water-bath. The reaction product was filtered off, washed with water, and dried in a desiccator over sulfuric acid. The product was N-butylbenzanilide (4.9 g, 96% of theoretical), m.p. 47-50°. M.p. after two recrystallizations from petroleum ether was 52.5-53.5°. Data in the literature: [17] b.p. 55°; [18] b.p. 47-48°.

For comparison, N-butylaniline and its benzoyl derivative were prepared. N-Butylaniline prepared from aniline and butyl bromide by Hickenbottom's method [19] had the following constants: b.p. 97-97.5° at 5 mm; d_4^{20} 0.9325; n_D^{20} 1.5350; found MR_D 49.81; calculated MR_D 48.38; EMR_D 1.43. The m.p. of N-butylbenzanilide obtained from this preparation and crystallized from petroleum ether was 53-54°. In admixture with the benzoyl derivative of N-butylaniline obtained from N-2-butenylaniline it melted at 52.5-53.5°.

Acetylation of N-2-Butenylaniline

Expt. 1. N-2-Butenylaniline (14.7 g, 0.1 mole) and 50 ml water were introduced into a flask provided with a mechanical stirrer. The stirrer was switched on, and 11.2 g acetic anhydride (0.11 mole) was added to the aqueous emulsion of amine. Stirring was continued for 30 minutes. Ether was then added, and the upper layer was separated. The aqueous layer was made alkaline with sodium carbonate and extracted with ether. The united ether extracts were washed with 5% sodium carbonate, then with water; they were dried with anhydrous potassium carbonate. The ether was distilled off, and the residue was fractionated. N-2-Butenylacetanilide (VIIIa) (14.1 g, 75% of theoretical) was obtained, with the following constants: b.p. 108-109° at 2 mm; d_4^{20} 1.0137; n_D^{20} 1.5324; found MR_D 57.87; calculated MR_D 57.15; EMR_D 0.72. It is a colorless viscous liquid. Data in the literature [13] b.p. 165-168° at 28 mm.

Found %: C 75.99, 75.74; H 8.09, 7.99; N 7.57, 7.54
$C_{12}H_{15}ON$. Calculated %: C 76.16; H 7.98; N 7.40

Expt. 2. N-2-Butenylaniline (17.7 g, 0.12 mole) dissolved in 40 ml acetic anhydride was introduced into a flask furnished with a reflux condenser. The mixture was heated on a boiling water bath for 3.5 hours. The acetic acid and acetic anhydride were then distilled off under reduced pressure (45 mm), and the residue was distilled at 2 mm. N-2-Butenylacetanilide (VIIIa) (21.2 g, 93% of theoretical) was obtained, with the following constants: b.p. 108-109° at 2 mm; d_4^{20} 1.0144; n_D^{20} 1.5328; found MR_D 57.87; calculated MR_D 57.15; EMR_D 0.72.

Oxidation of N-2-Butenylacetanilide to N-Acetyl-N-phenylglycine

A solution of potassium permanganate (4.7 g, 0.03 mole) in 325 ml dry acetone was added over 2 hours with constant stirring to a solution of N-2-butenylacetanilide (1.89 g, 0.01 mole) in 100 ml dry acetone. On the next day the precipitate was filtered off, washed on the filter with acetone, and extracted with 50 ml water. The aqueous extract was extracted with chloroform and acidified with diluted hydrochloric acid. The precipitate was filtered off, washed with cold water, and dried in a desiccator over sulfuric acid. N-Acetyl-N-phenylglycine (0.77 g, 40% of theoretical), m.p. 189-192°, was obtained. M.p. after recrystallization from hot water was 193.5-195°. In admixture with N-acetyl-N-phenylglycine (m.p. 193-195°) obtained by the acetylation of N-phenylglycine it melted at 193.5-195°.

Hydrolysis of N-2-Butenylacetanilide with Hydrochloric Acid

N-2-Butenylacetanilide (18.9 g, 0.1 mole) and 250 ml conc. HCl were introduced into a flask fitted with a reflux condenser. The mixture was boiled for 6 hours. It was then cooled, diluted with 250 ml water, and rendered alkaline with 40% aqueous caustic soda. The oil that separated was extracted with ether, and the ethereal solution was washed with water and then dried with anhydrous sodium sulfate. The ether was driven off, and the residue was vacuum-distilled. A fraction (10.9 g) of b.p. 120-125° at 1 mm was obtained. After a short time, this fraction partially crystallized. The crystals were filtered off and washed with absolute ether. The crystals (5.8 g, 35% of theoretical) were almost colorless; m.p. 59-61°. M.p. after recrystallization from cyclohexane was 60.5-61.5°. Data in the literature: [2] m.p. 60.5-61.5°.

	Found %:	C 72.69, 72.75;	H 8.97, 8.99;	N 8.47, 8.47
$C_{10}H_{13}ON$.	Calculated %:	C 72.89;	H 9.15;	N 8.48

Benzoylation of N-2-Butenylaniline

N-2-Butenylaniline (5.9 g, 0.04 mole) was emulsified in a 10% solution of caustic soda (40 g of solution). Benzoyl chloride (8.4 g, 0.06 mole) was added to the emulsion in 5 portions over 20 minutes with energetic shaking. Excess benzoyl chloride was hydrolyzed by warming on the water bath. The benzoylation product was filtered off, washed with water, and dried in a desiccator over sulfuric acid. N-2-Butenylbenzanilide (VIIIb) (9.6 g, 95% of theoretical) was obtained. M.p. 85-89°; m.p. after two recrystallizations from ethanol was 90-91°. Data in the literature: [18] b.p. 204-207° at 13 mm; [2] m.p. 90-91°.

	Found %:	C 81.17, 81.14;	H 6.89, 6.79;	N 5.30, 5.28
$C_{17}H_{17}ON$.	Calculated %:	C 81.24;	H 6.82;	N 5.57

Hydrolysis of N-2-Butenylbenzanilide with Hydrochloric Acid

N-2-Butenylbenzanilide (12.6 g, 0.05 mole) and 125 ml conc. HCl were introduced into a flask fitted with a reflux condenser, and the mixture was boiled for 8 hours. It was then cooled, diluted with 125 ml water, and extracted with ether to remove benzoic acid (yield 5.8 g). The acid solution was rendered alkaline with caustic soda, and the oil that separated was dissolved in ether. The ethereal solution was dried with anhydrous sodium sulfate; the ether was driven off, and the residue was vacuum-distilled. A fraction (5.1 g) of b.p. 131-137° at 3 mm was obtained; it partially crystallized out on standing. The crystals were filtered off and washed with absolute ether. The product was the hydroxy amine $C_{16}H_{15}ON$ (2.5 g, 30% of theoretical), m.p. 59-61°. M.p. after recrystallization from cyclohexane was 60.5-61.5°.

In conclusion I express my deep gratitude to A.N.Nesmeyanov for his valuable advice and for his constant interest in my work.

SUMMARY

1. It has been found that when 3,6-dihydro-2-phenyl-1,2,2H-oxazine is reduced by means of zinc dust and acetic acid under severe conditions, 1-phenyl-3-pyrroline is formed.

2. It has been found that when 3,6-dihydro-2-phenyl-1,2,2H-oxazine is reduced by means of sodium and alcohol, N-2-butenylaniline is formed.

3. It has been shown that when 3,6-dihydro-2-phenyl-1,2,2H-oxazine is reduced to give 1-phenyl-3-pyrroline, 4-phenylamino-2-buten-1-ol is formed as an intermediate product.

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* See Consultants Bureau translation, p. 339.

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REDUCTION OF 1-PHENYLPYRROLE

Yu. A. Arbuzov and M. M. Garburg

Addition of hydrogen to the pyrrole nucleus proceeds in two stages: first, dihydro derivatives are formed, and then tetrahydro derivatives. Reduction of the pyrrole nucleus with addition of two hydrogen atoms and formation of pyrrolines has been described in adequate detail only for pyrrole itself.

The oldest method for the reduction of pyrrole to pyrroline is that of Ciamician [1], which consists in reduction with zinc dust and acetic acid, with application of heat. Knorr and Rabe [2] found that the reduction of pyrrole to pyrroline goes better when zinc dust and hydrochloric acid are used. Zelinsky and Yuryev [3] proposed the use of zinc-palladium and hydrochloric acid for this purpose. Reduction of pyrrole homologs to pyrrolines has been described for 1-methylpyrrole [4], 2,3-dimethylpyrrole [5], 2,4-dimethylpyrrole [2], 2,5-dimethylpyrrole [2,29], and 1,2,5-trimethylpyrrole [2]. On the basis of the propensity shown by compounds having two conjugated double bonds to give 1,4-addition reactions, the dihydro derivatives obtained by the reduction of pyrrole and its homologs were regarded as 2,5-dihydro derivatives (3-pyrrolines). This was shown to be so for pyrroline itself by Treibs and Dinelli [6], who obtained iminodiacetic acid by the ozonolysis of pyrroline.*

Later, several papers were published in which descriptions were given of the reduction by zinc dust and hydrochloric acid of certain C-arylpyrroles to 2-pyrrolines. Thus Sohn [7] found that reduction of 2-methyl-4-phenylpyrrole yields 2-methyl-4-phenyl-2-pyrroline. According to Sohn's results [8], 4-methyl-2-phenylpyrrole also unites with hydrogen in the 4,5-positions with formation of 4-methyl-2-phenyl-2-pyrroline. Sohn gives the conjugation of the double bonds of the benzene and pyrrole nuclei as the explanation of the reduction of C-arylpyrroles to 2-pyrrolines. Wibaut [9], by reducing 2-phenylpyrrole, obtained a dihydro derivative to which he ascribed the structure of 5-phenyl-2-pyrroline. In a further communication [10], Wibaut stated that by the reduction of 2-(p-chlorophenyl)pyrrole, 2-(m-chlorophenyl)pyrrole, 2-(o-chlorophenyl)pyrrole, and 2-(m-bromophenyl)pyrrole, 2,3-dihydro derivatives are again formed. By the reduction of 1-methyl-2-(β-pyridyl)pyrrole (nicotyrine) Wibaut [11] obtained dihydronicotyrine, to which Spath and Wibaut [12] ascribed the structure of 1-methyl-2-(β-pyridyl-2-pyrroline (N-methylmyosmine). However, in 1950 Haines and Eisner [13] synthesized N-methylmyosmine and found that it is not identical with Wibaut's dihydronicotyrine. In 1951, King [14] found that, on ozonolysis of 2-phenylpyrroline prepared by the reduction of 2-phenylpyrrole with zinc dust and hydrochloric acid, α-phenyl-α,α'-iminodiacetic acid is formed. Hence, it was established that 2-phenylpyrrole unites with hydrogen in the 2,5-positions with formation of 2-phenyl-3-pyrroline. It must be supposed that in the reduction of nicotyrine a 3-pyrroline derivative (1-methyl-2-β-pyridyl-3-pyrroline) is formed.**

From the above it follows that also the remainder of the work cited on the reduction of 2-arylpyrroles to 2-pyrrolines requires critical review. The aim of the present work is to investigate the reduction of 1-phenylpyrrole and to study the possibility of preparing by this means 1-phenyl-3-pyrroline, which was prepared by one of us [15] by the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine (nitrosobenzene adduct of 1,3-butadiene) by means of zinc dust and acetic acid.

1-Phenylpyrrole is generally prepared by thermal decomposition of aniline mucate [16-21]. We obtained 1-phenylpyrrole in 56% yield by the thermal decomposition of aniline mucate in presence of aluminum oxide.*** When the decomposition was carried out in absence of aluminum oxide, the yield of 1-phenylpyrrole was only 42%. For 1-phenylpyrrole, reduction with addition of two hydrogen atoms has not been described. Only its catalytic reduction to 1-phenylpyrrolidine [23] or to 1-cyclohexylpyrrolidine [19,22,23] has been described. In view of the readiness with which hydrogen unites with pyrrole and its homologs, our trials on the reduction of

* Evans [28] has found recently that when pyrrole homologs are reduced with zinc dust and hydrochloric acid, a mixture of isomeric pyrrolines is formed. Thus, 2,5-dimethyl-3-pyrroline (about 80%) and 2,5-dimethyl-1-pyrroline (about 20%) were isolated from the reduction products of 2,5-dimethylpyrrole. Reduction of 1,2,5-trimethylpyrrole and of 2-methylpyrrole led also to mixtures of isomeric dihydro derivatives.

** In a recent paper, Wibaut [30] considers that the structure of 1-methyl-2-(β-pyridyl)-3-pyrroline is the most probable one for dihydronicotyrine.

*** Aluminum oxide has been employed by Chichibabin [24] in the preparation of 1-(α-pyridyl)pyrrole from a mixture of α-aminopyridine and mucic acid.

1-phenylpyrrole were made under the mildest conditions possible. Nevertheless, it was found that, when treated with zinc dust and acetic acid, both cold and hot, 1-phenylpyrrole did not unite with hydrogen.

Treatment of 1-phenylpyrrole with zinc dust and hydrochloric acid at 60-75° led to the formation of an oil, which consisted of a mixture of reduction products. Elementary analysis of the main fraction of the reduction product (b.p. 90-92° at 3 mm) showed that under these conditions of reduction four hydrogen atoms add to the 1-phenylpyrrole molecule. Similar results were obtained by the action on 1-phenylpyrrole of zinc dust with hydrochloric and acetic acids at 50-65° and at 40-50°. The mixture of reduction products was subjected to benzoylation, and a liquid tertiary amine and a crystalline benzoylation product were isolated. The constants of the tertiary amine, after purification by vacuum-distillation, showed it to be 1-phenylpyrrolidine. For comparison, some 1-phenylpyrrolidine was synthesized from 1,4-dibromobutane and aniline, and picrates were prepared from both compounds. A mixed m.p. on the picrates showed no depression. Thus, the tertiary amine that we obtained by the reduction of 1-phenylpyrrole was 1-phenylpyrrolidine.

After recrystallization from ethanol, the crystalline benzoylation product melted at 90-91°. Elementary analysis of this substance showed it to have the composition $C_{17}H_{17}ON$. The substance was subjected to hydrolysis by means of hydrochloric acid, and a crystalline product, m.p. 60.5-61.5° was obtained. Elementary analysis of the substance showed it to have the composition $C_{10}H_{15}ON$. Hence, as a result of hydrolysis with hydrochloric acid the substance gave not the expected amine of composition $C_{10}H_{13}N$, but the product formed by addition of a molecule of water to this amine.

Hydrolysis of the crystalline benzoylation product with alcoholic alkali yielded a liquid amine having constants close to those of N-2-butenylaniline, which was obtained by one of us [15] by the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine by means of sodium and alcohol. For comparison, the benzoyl derivative of N-2-butenylaniline was prepared; it melted at 90-91°. A mixture of the two compounds melted without depression. Hence, the crystalline benzoylation product was the benzoyl derivative of N-2-butenylaniline. The formation of a compound of composition $C_{10}H_{15}ON$ by hydrolysis of the benzoyl derivative of N-2-butenylaniline by means of hydrochloric acid may be explained by the occurrence, simultaneously with hydrolysis, of addition of the elements of water at the double bond.*

By the benzoylation of the low-boiling fraction (b.p. up to 92° at 4 mm) obtained by the reduction of 1-phenylpyrrole by means of zinc dust and hydrochloric and acetic acids at 40-50°, benzanilide, m.p. 162-163°, was obtained.

As the above-given results of our experiments show, reduction of 1-phenylpyrrole under the conditions that we have studied leads to the formation of 1-phenylpyrrolidine, N-2-butenylaniline, and aniline. We have found that 1-phenyl-3-pyrroline is not reduced by zinc dust in conjunction with hydrochloric and acetic acids at 40-50°, and this result excludes the possibility of the intermediate formation of 1-phenyl-3-pyrroline as a stage in the reduction of 1-phenylpyrrole. There remains the possibility that the first stage in the reduction of 1-phenylpyrrole is the formation of 1-phenyl-2-pyrroline.

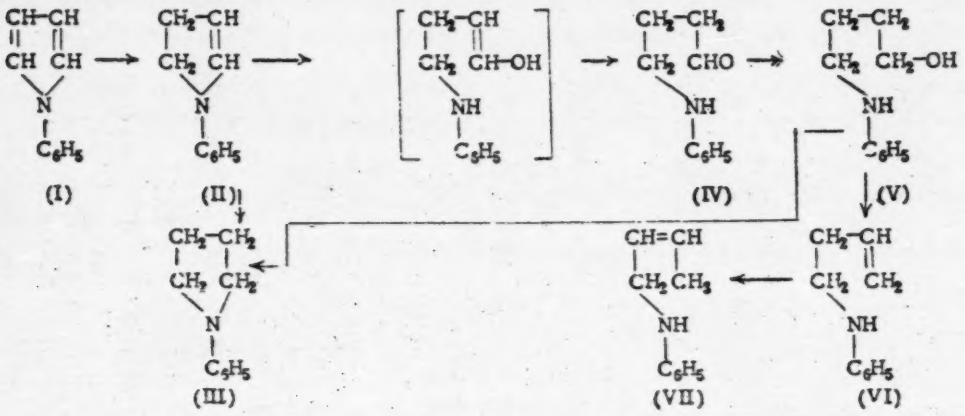
It has been established by the work of Lipp and Markwalder that N-phenyl-2-piperideines and N-phenyl-2-pyrrolines can exist only in the form of salts. Thus, Lipp [26] found that, when aniline reacts with 6-bromo-2-hexanone, the hydrobromide of 1,2,3,4-tetrahydro-6-methyl-1-phenylpyridine is formed. When attempts were made to isolate the free base from the hydrobromide, hydrolytic opening of the piperideine ring occurred, and 6-phenylamino-2-hexanone was formed. When the 6-phenylamino-2-hexanone was treated with acids, the piperideine ring was reformed to give salts of 1,2,3,4-tetrahydro-6-methyl-1-phenylpyridine. By the reduction of 6-phenylamino-2-hexanone with tin and hydrochloric acid, Lipp obtained 2-methyl-1-phenylpiperidine. Markwalder [27] showed that, in a similar way, attempts made to isolate the free base from the hydrobromide of 2-methyl-1-phenyl-2-pyrroline lead to hydrolytic opening of the pyrroline ring and formation of 5-phenylamino-2-pentanone, which, under the action of acids, is again converted into salts of 2-methyl-1-phenyl-2-pyrroline. By the reduction of 5-phenylamino-2-pentanone by means of tin and hydrochloric acid, 2-methyl-1-phenylpyrrolidine was obtained.

On the basis of all these considerations it may be supposed that the formation of 1-phenylpyrrolidine and N-2-butenylaniline in the reduction of 1-phenylpyrrole proceeds in the following way. 1-Phenylpyrrole (I) is first

* A similar result was obtained by Mumm and Moller [25] in the hydrolysis of the benzoyl derivative of α-methylallylaniline. Instead of the expected α-methylallylaniline, a hydroxy amine of composition of $C_{10}H_{15}ON$ was obtained.

reduced to 1-phenyl-2-pyrroline (II), which, on the one hand, unites with two atoms of hydrogen giving 1-phenylpyrrolidine (III) and, on the other hand, undergoes hydrolytic decyclization with formation of γ-phenylaminobutyraldehyde (IV). The aldehyde (IV) is reduced further to 4-phenylamino-1-butanol (V), which is dehydrated to give N-3-butenylaniline (VI), which isomerizes into N-2-butenylaniline (VII). 1-Phenylpyrrolidine (III) can be formed also in another way, namely by cyclodehydration of 4-phenylamino-1-butanol (V).

It may be supposed that aniline is formed by the splitting of N-2-butenylaniline by hydrogenation. Further experimental study of the reaction will be necessary in order to determine whether this explanation of the mechanism of the reduction of 1-phenylpyrrole is correct.



EXPERIMENTAL

Preparation of 1-Phenylpyrrole

Expt. 1. Mucic acid (42 g; 0.2 mole) was added with constant stirring to aniline (37.2 g; 0.4 mole) heated to 150-160°. The mixture was heated at 140-150° for 1 hr and was allowed to stand for several days. It had then grown hard and readily broke down into a light-yellow powder. The aniline mucate obtained was carefully ground with aluminum oxide (42 g), and the mixture was transferred to a 200 ml round-bottomed flask fitted with a condenser arranged for distillation. The flask was heated on an oil bath. Distillation commenced at a bath temperature of 250° and terminated at 340°. The main portion of the distillate came over at a bath temperature of 270-320°. A residue of aluminum oxide impregnated with resin remained in the flask. The distillate was acidified with dilute hydrochloric acid, and the 1-phenylpyrrole was steam-distilled off, filtered off, washed with water, and dried in a desiccator over sulfuric acid (15.8 g; 66%. M.p. 58-59°). M.p. after sublimation: 61-62°.

Expt. 2. Aniline mucate was prepared from mucic acid (42 g; 0.2 mole) as in expt. 1. The salt obtained was introduced into a 200 ml round-bottomed flask, which was heated on an oil bath. Distillation commenced at 220° and finished at 320°. 1-Phenylpyrrole was isolated from the distillate as described above (11.8 g; 42%. M.p. 58-59°).

Reduction of 1-Phenylpyrrole by Means of Zinc Dust in Conjunction with Hydrochloric and Acetic Acids at 50-65°

Zinc dust (120 g) and conc. HCl (120 g) were added in small portions with energetic shaking to a solution of 1-phenylpyrrole (20 g) in glacial acetic acid (200 ml). The temperature of the reaction mixture was constantly maintained within the range 50-65°. Addition of zinc and hydrochloric acid occupied $1\frac{1}{2}$ hr. During the following $1\frac{1}{2}$ hr, the reaction mixture was agitated vigorously and was warmed on the water-bath to 50-65°. The mixture was then cooled, rendered alkaline with caustic soda, and steam-distilled. The yellow oil that went over into the distillate was extracted with ether, and the ether extract was dried over fused caustic potash. The ether was driven off, and the residue was dried by means of barium oxide at 110-120° for 6 hrs and then fractionated at 6 mm. The following fractions were obtained:

Fraction 1, b.p. to 100° – 1.3 g
Fraction 2, b.p. 100-102.5° – 4.7 g; d_4^{20} 0.9792; n_D^{20} 1.5648
Fraction 3, b.p. 102.5-105° – 1.2 g

Analysis of Fraction 2

	Found %:	C 81.93; 81.95;	H 8.79; 8.81;	N 9.50; 9.36
$C_{16}H_{13}N$.	Calculated %:	C 81.59;	H 8.90;	N 9.51
$C_{16}H_{11}N$.	Calculated %:	C 82.71;	H 7.64;	N 9.65

In order to obtain sufficient material, the reduction of 1-phenylpyrrole under these conditions was repeated several times. When the steam-distilled and dried product of the reduction reaction was vacuum-distilled, the fraction of b.p. 92-102° at 5 mm was collected, and this was subjected to further investigation.

Benzoylation of the Fraction of b.p. 92-102° (5 mm). The substance (16 g) was emulsified in 10% caustic soda solution (70 ml), and over an hour with vigorous agitation benzoyl chloride (14 g) was added in 5 portions. The excess of benzoyl chloride was hydrolyzed by warming. The upper layer (a mixture of an oil and a crystalline substance) was separated, washed with water, and then extracted with 10% hydrochloric acid. The crystalline substance was filtered off, washed with water, and dried in a desiccator over sulfuric acid.

Isolation of 1-Phenylpyrrolidine. The hydrochloric acid extract, the filtrate, and the washings were united. The resulting solution was rendered alkaline by means of caustic soda, and the oil that separated was extracted with ether. The ether extract was dried by means of fused caustic potash. The residue remaining after the ether had been driven off was vacuum-distilled. The product was 1-phenylpyrrolidine (8.3 g) having the following constants: b.p. 129-131° at 16 mm; d_4^{20} 1.0172; n_D^{20} 1.5839.

Picrate of 1-Phenylpyrrolidine. A warm ethereal solution of picric acid (2.29 g; 0.01 mole) was added to an ethereal solution of 1-phenylpyrrolidine (1.47 g; 0.01 mole). A finely crystalline precipitate of the picrate immediately began to appear. It was filtered off and washed with ether (3.64 g; m.p. 114-115°). M.p. after recrystallization from ethanol: 116-117°.

1-Phenylpyrrolidine prepared by us from 1,4-dibromobutane and aniline had the following constants: b.p. 129-130° at 16 mm; d_4^{20} 1.0145; n_D^{20} 1.5820. The picrate prepared from this preparation and recrystallized from ethanol melted at 116-117°. In admixture with the picrate of 1-phenylpyrrolidine obtained by the reduction of 1-phenylpyrrole it melted without depression.

The Benzoyl Derivative of N-2-Butenylaniline. The crystalline benzoylation product (11 g) melted at 83-89°. After three recrystallizations from ethanol, 6.8 g of the benzoyl derivative of N-2-butenylaniline, m.p. 90-91°, was obtained.

	Found %:	C 81.08; 81.05;	H 6.91; 6.98;	N 5.48; 5.28
$C_{17}H_{17}ON$.	Calculated %:	C 81.24;	H 6.82;	N 5.57

The benzoyl derivative of N-2-butenylaniline readily dissolves on warming in ethanol, benzene, acetone, and ether; it crystallizes in prisms from ethanol. The N-2-butenylaniline prepared by one of us [15] by the reduction of 3,6-dihydro-2-phenyl-1,2,2H-oxazine with sodium and alcohol was benzoylated. The benzoyl derivative, after recrystallization from ethanol, melted at 90-91°. In admixture with the benzoyl derivative of N-2-butenylaniline obtained by the reduction of 1-phenylpyrrole, it melted without depression.

Hydrolysis of the Benzoyl Derivative of N-2-Butenylaniline by means of Hydrochloric Acid. The benzoyl derivative (10 g) and conc. HCl (100 ml) were introduced into a flask fitted with a reflux condenser. The mixture was boiled for 12 hrs. It was then cooled, diluted twice with water, and the benzoic acid was extracted with ether. The acid solution was rendered alkaline with caustic soda, and the oil that separated was extracted with ether. The ether extract was dried with fused caustic potash. The residue after removal of ether was distilled over under 12 mm pressure. The following fractions were collected:

Fraction 1, b.p. to 155° — 1.6 g
Fraction 2, b.p. 155-165° — 3.1 g

Fraction 2 partially crystallized out. The crystals were filtered off and washed with absolute ether. A substance (2.0 g) of m.p. 59-61° was obtained. M.p. after recrystallization from ethanol: 60.5-61.5°.

	Found %:	C 73.06; 73.10;	H 9.22; 9.06;	N 8.24; 8.07
$C_{18}H_{15}ON$.	Calculated %:	C 72.69;	H 9.15;	N 8.48

Hydrolysis of the Benzoyl Derivative of N-2-Butenylaniline with Alcoholic Alkali. The benzoyl derivative (8 g) and a solution of caustic potash (5 g) in isoamyl alcohol (20 ml) were introduced into a flask fitted with reflux condenser. The mixture was boiled for 3 hrs. The contents of the flask were cooled and diluted with ether; potassium benzoate was extracted with water. The ethereal solution was extracted with 20% hydrochloric acid. The acid extract was washed with ether, rendered alkaline with caustic soda, and the oil that separated was extracted with ether. The ethereal solution was dried with fused caustic potash, the ether was driven off, and the residue was fractionated. N-2-Butenylaniline (1.5 g) was obtained; it had the following constants: b.p. 93-95° at 4 mm; d_4^{23} 0.9573; n_D^{20} 1.5554. N-2-Butenylaniline prepared from 3,6-dihydro-2-phenyl-1,2,2H-oxazine [15] had the following constants: b.p. 89-90° at 3 mm; d_4^{20} 0.9613; n_D^{20} 1.5587.

Reduction of 1-Phenylpyrrole by means of Zinc Dust in conjunction with Hydrochloric and Acetic Acids at 40-50°

Zinc dust (100 g) and conc. HCl (100 ml) were added in small portions at a time over 1½ hr with vigorous agitation to a solution of 1-phenylpyrrole (20 g) in glacial acetic acid (200 ml). The temperature of the reaction mixture was maintained in the range 40-50°. During the following 1½ hr, the reaction mixture was vigorously agitated and kept at 40-50° on a water-bath. The mixture was cooled, made alkaline with caustic soda, and steam-distilled. Further treatment was carried out as in the previous experiment. In the fractionation of the reduction product under 4 mm pressure, the following fractions were collected:

Fraction 1, b.p. to 92° — 1.4 g
Fraction 2, b.p. 92-96° — 8.1 g

Benzoylation of Fraction 1. The substance (1.4 g) was emulsified in 10% caustic soda solution (10 ml). Benzoyl chloride (2.1 g) was added to the emulsion, and the mixture was agitated for 20 min. The crystalline benzoylation product was filtered off, washed with water, and dried in a desiccator over sulfuric acid (2.5 g; m.p. 145-155°). After four recrystallizations from ethanol, 1.2 g of benzanilide, m.p. 162-163°, was obtained.

Found %: C 79.06; 79.33; H 5.62; 5.69; N 6.82; 6.79
$C_{13}H_{11}ON$. Calculated %: C 79.16; H 5.62; N 7.10

Benzoylation of Fraction 2. The substance (8.0 g) was emulsified in a 10% solution of caustic soda (80 ml), and benzoyl chloride (7.0 g) was added to the emulsion with agitation in three portions. From the reaction products, 1-phenylpyrrolidine (5.4 g) and the benzoyl derivative of N-2-butenylaniline (2.7 g; m.p. 90-91°) were isolated.

Reduction of 1-Phenylpyrrole by means of Zinc Dust and Hydrochloric Acid at 60-75°

Zinc dust (50 g) was added in small portions at a time with vigorous shaking to an emulsion of 1-phenylpyrrole (20 g) in conc. HCl (100 ml) heated to 60°. The zinc dust was added over 4 hrs. Then, further zinc dust (100 g) and conc. HCl (300 ml) were added over 4 hrs. The temperature of the mixture was maintained constantly in the range 60-75°. The reaction mixture was cooled, made alkaline with caustic soda, and steam-distilled. Further treatment was carried out as in the previous experiments. As a result of fractionation at 3 mm, the following fractions were obtained:

Fraction 1, b.p. to 90° — 1.0 g
Fraction 2, b.p. 90-92° — 4.4 g; d_4^{20} 0.9903; n_D^{20} 1.5692
Fraction 3, b.p. above 92° — 0.8 g

Analysis of Fraction 2

Found %: C 81.58; 81.62; H 8.88; 8.77; N 9.52; 9.66
$C_{10}H_{13}N$. Calculated %: C 81.63; H 8.90; N 9.51
$C_9H_{11}N$. Calculated %: C 82.71; H 7.64; N 9.65

From the benzoylation products in Fraction 2, 1-phenylpyrrolidine and the benzoyl derivative of N-2-butenylaniline, m.p. 90-91°, were isolated.

SUMMARY

1. An investigation has been made into the reduction of 1-phenylpyrrole by means of zinc dust and hydrochloric acid at 60-75° and by means of zinc dust in conjunction with hydrochloric and acetic acids at 40-60° and at 50-65°.

2. It has been found that, when 1-phenylpyrrole is reduced under the conditions used in this work, it unites with four atoms of hydrogen with formation of 1-phenylpyrrolidine and N-2-butenylaniline.

3. An explanation has been proposed for the mechanism of the reduction of 1-phenylpyrrole involving the intermediate formation of 1-phenyl-2-pyrroline.

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BRIEF COMMUNICATIONS

SYNTHESIS AND PROPERTIES OF ALLYLSILANES: TRIALLYL-α-NAPHTHYLSILANE, TRIALLYLCYCLOHEXYLSILANE, TRIALLYLBUTYLSILANE, AND ALLYLTRIBUTYLSILANE

A. D. Petrov and L. L. Shchukovskaya

Sila-hydrocarbons of the type $(CH_2=CH-CH_2)_x \cdot SiR_{4-x}$ are of considerable interest because of the comparative ease with which they polymerize and undergo copolymerization [1] with vinyl-type compounds (styrene, vinyl chloride, acrylates). However, very few representatives of this series have yet been synthesized; also, all the known sila-hydrocarbons contain only aliphatic radicals (R). Whitmore [2] obtained $(CH_2=CH-CH_2) \cdot Si(CH_3)_3$; Yakovlev [3] $(CH_2=CH-CH_2)_2 \cdot Si(C_2H_5)_2$; Petrov and Mironov [4] $(CH_2=CH-CH_2) \cdot Si(C_2H_5)_3$; Post [5] $HSi(CH_2-CH=CH_2)_3$ and in one U.S. patent [6], a description is given of the synthesis and properties of $Si(CH_2-CH=CH_2)_4$ (b.p. 102-103° at 15 mm; d_4^{20} 0.8353; n_D^{20} 1.4864).

EXPERIMENTAL

In this investigation we have prepared for the first time the allylsilanes indicated above, and we have also repeated the synthesis of $Si(CH_2-CH=CH_2)_4$. In the first two syntheses we used the usual method for the preparation of sila-hydrocarbons — via an alkyl- or aryl-magnesium halide, the reaction being begun in ether and completed by heating in ligroin (fraction of b.p. 130-160°). In subsequent syntheses the reaction was carried out in ether.

Triallyl-α-naphthylsilane $\alpha\text{-}C_{10}H_7Si(CH_2-CH=CH_2)_3$. Triethoxy-α-naphthylsilane $\alpha\text{-}C_{10}H_7Si(OC_2H_5)_3$ and allyl bromide, taken in a molar ratio of 1:4, were poured into absolute ether containing magnesium. After the complex had been broken down by means of ammonium chloride, a sila-hydrocarbon containing 35% of the initial triethoxynaphthylsilane was obtained. The pure sila-hydrocarbon was obtained only after a further treatment with allylmagnesium bromide and heating in ligroin. Yield 60% of theoretical.

Triallylcyclohexylsilane $C_6H_{11}Si(CH_2-CH=CH_2)_3$. This was synthesized in the same way. Yield 42% of theoretical. The original cyclohexyltriethoxysilane $(C_6H_{11}Si(OC_2H_5)_3$ had the following constants: b.p. 101-102° at 7 mm; n_D^{20} 1.4280; d_4^{20} 0.9444.

	Found %:	C 58.44; 58.69;	H 10.72; 10.54; Si 11.32; 11.57
$C_{12}H_{22}SiO_3$.	Calculated %:	C 58.49;	H 10.64; Si 11.39

Triallylbutylsilane $C_4H_9Si(CH_2-CH=CH_2)_3$. This was prepared by the action of n-butyltrichlorosilane on allylmagnesium bromide. After the ether had been driven off, the residue in the flask was heated on a boiling water bath. The reaction product was decomposed with ammonium chloride, and the sila-hydrocarbon was purified by heating with metallic sodium on the water-bath. Yield 54% of theoretical.

Allyltributylsilane $(n\text{-}C_4H_9)_3Si \cdot CH_2-CH=CH_2$. This was prepared by adding a mixture of allyl bromide and tributylchlorosilane to magnesium. The product was purified as indicated above. Yield 74% of theoretical.

Tributylchlorosilane $(n\text{-}C_4H_9)_3SiCl$. This was synthesized by Whitmore's method [7]; the yield was 74.2%; b.p. 124.5° at 8 mm; n_D^{20} 1.4471; d_4^{20} 0.8763.

	Found %:	Cl 14.57; 14.47
$(n\text{-}C_4H_9)_3SiCl$.	Calculated %:	Cl 15.08

Hexabutyldisiloxane had the following properties: b.p. 198-200° at 12 mm; n_D^{20} 1.4455; d_4^{20} 0.8553.

	Found %:	Si 13.84
$n\text{-}(C_4H_9)_3Si_2O$.	Calculated %:	Si 13.52

TABLE

Properties of Allylsilanes

α-$C_{18}H_{32}Si(CH_2{-}CH{=}CH_2)_3$ b.p. 194-195° at 10 mm; n_D^{20} 1.5872; d_4^{20} 0.9928	Found %: C 81.56; 81.55; H 8.36; 8.16; Si 10.09; 10.13 $C_{19}H_{32}Si$. Calculated %: C 81.95; H 7.96; Si 10.09
$C_6H_{11}Si(CH_2{-}CH{=}CH_2)_3$ b.p. 127-129° at 13 mm; n_D^{20} 1.4790; d_4^{20} 0.8659; MR_D(found) 76.7; MR_D(calcd) 77.36	Found %: C 77.08; H 11.81; Si 11.18 $C_{15}H_{26}Si$. Calculated %: C 76.92; H 11.10; Si 12.0
n-$C_4H_9Si(CH_2{-}CH{=}CH_2)_3$ b.p. 108° at 11 mm; n_D^{20} 1.4722; d_4^{20} 0.8200; MR_D (found) 71.05; MR_D (calcd) 70.33	Found %: C 75.31; H 11.67; Si 12.91 $C_{15}H_{28}Si$. Calculated %: C 75.0 ; H 11.54; Si 13.46
$(n\text{-}C_4H_9)_3SiCH_2{-}CH{=}CH_2$ b.p. 145° at 12 mm; n_D^{20} 1.4534; d_4^{20} 0.8031; MR_D (found) 80.83; MR_D (calcd) 80.50	Found %: C 74.73; 74.77; H 13.48; 13.50; Si 10.78; 11.18 $C_{15}H_{32}Si$. Calculated %: C 75.0; H 13.30; Si 11.66
$Si(CH_2{-}CH{=}CH_2)_4$ b.p. 90.5° at 10 mm; n_D^{20} 1.4840; d_4^{20} 0.8345; MR_D (found) 65.82; MR_D (calcd) 65.25	Found %: C 75.80; 75.63; H 10.66; 10.74 $C_{12}H_{20}Si$. Calculated %: C 75.0 ; H 10.04

Tetraallylsilane $Si(CH_2{-}CH{=}CH_2)_4$ was prepared by adding a mixture of tetrachlorosilane and allyl iodide to magnesium. The ether was driven off, and the product was distilled off without first breaking down the complex. Yield 37% of theoretical. The properties of the silanes that we prepared are given in the table.

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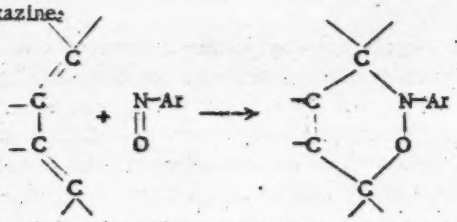
THE REACTIONS OF DIENIC HYDROCARBONS WITH NITROSO COMPOUNDS

ADDITION OF 2,3-DIMETHYL-1,3-BUTADIENE, OF 1-PHENYL-1,3-BUTADIENE, AND OF BI-1-CYCLOHEXEN-1-YL TO AROMATIC NITROSO COMPOUNDS

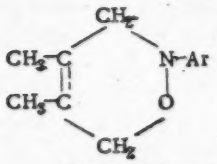
Yu. A. Arbuzov, N. L. Fedyukina, V. V. Shabyrina, and R. I. Shepeleva

In the previous papers [1,2] it was shown that 1,3-butadiene, 1,3-pentadiene, and 2,4-hexadiene add on to aromatic nitroso compounds according to the scheme of the diene synthesis with formation of derivatives of 3,6-dihydro-1,2,2H-oxazine:

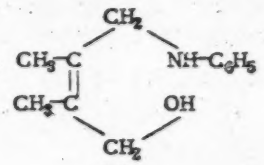


It was to be expected that the addition reaction between dienic hydrocarbons and nitroso compounds leading to the formation of 3,6-dihydro-1,2,2H-oxazine derivatives would have a general character. The experimental data that we bring forward in this paper confirm this supposition.

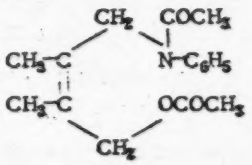
We have prepared addition products of aromatic nitroso compounds with 2,3-dimethyl-1,3-butadiene, trans-1-phenyl-1,3-butadiene, and bi-1-cyclohexen-1-yl. In the experiments in which 2,3-dimethyl-1,3-butadiene was added to nitroso compounds, ether was used as solvent. Two compounds were formed in the reaction between 2,3-dimethyl-1,3-butadiene and nitrosobenzene. The first is almost insoluble in ether and consists of colorless glistening needles, m.p. 153-155° (dec.). This substance begins to separate on the walls of the reaction flask soon after the addition of the dimethylbutadiene to the ethereal solution of nitrosobenzene, while the reaction mixture still has a green color. The nature of the substance of m.p. 153-155° has not yet been established. The second substance, which is 3,6-dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine (Ia), is soluble in ether. This substance was obtained in 66% yield and has b.p. 125-126° at 3 mm and m.p. 39.5-40.5°. The reduction of 3,6-dihydro-4,5-dimethyl-2-phenyl-1,2-2H-oxazine (Ia) with zinc dust and glacial acetic acid leads to the formation of 2,3-dimethyl-4-phenylamino-2-buten-1-ol (II), b.p. 154.5-155° at 2 mm. Acetylation of the amino alcohol (II) with acetic anhydride gives the diacetyl derivative (III), which has b.p. 157-158° at 1 mm.



(Ia) Ar = phenyl
(Ib) Ar = p-tolyl



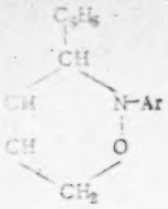
(II)



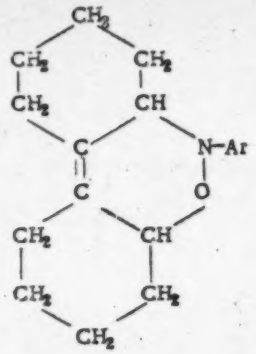
(III)

In the reaction between 2,3-dimethyl-1,3-butadiene and p-nitrosotoluene, the reaction conditions being the same as in the reaction with nitrosobenzene, the ether-insoluble substance was not obtained. From the reaction products, 3,6-dihydro-4,5-dimethyl-2-(p-tolyl)-1,2,2H-oxazine (Ib), m.p. 62-63°, was isolated with a yield of 55%.

The reaction of 1-phenyl-1,3-butadiene with nitrosobenzene was carried out in ethanol and in pyridine. When an ethanol medium was used, the adduct (IVa or Va), m.p. 84.5-85°, was obtained with a yield of 85%. When a pyridine medium was used, the yield of the adduct was only 55%. In the reaction of 1-phenyl-1,3-butadiene with o-nitrosotoluene in ethanol, an adduct (IVb or Vb), m.p. 46-47°, was obtained in 80% yield. In the reaction of 1-phenyl-1,3-butadiene with p-nitrosotoluene in ethanol solution, an 80% yield of the adduct (IVc) or (Vc), m.p. 66-67°, was obtained.



(Va) Ar = phenyl
(Vb) Ar = o-tolyl
(Vc) Ar = p-tolyl



(VIa) Ar = phenyl
(VIb) Ar = p-tolyl

The addition of bi-1-cyclohexen-1-yl to nitroso compounds were carried out in benzene. In the reaction of bicyclohexenyl with nitrosobenzene, a 26% yield was obtained of 1,2,3,4,4a,6a,7,8,9,10-decahydro-6-phenyl-6H-dibenz[c,e]-o-oxazine (VIa), m.p. 100-101°. In the reaction of bicyclohexenyl with p-nitrosotoluene, a 30% yield was obtained of 1,2,3,4,4a,6a,7,8,9,10-decahydro-6-(p-tolyl)-6H-dibenz[c,e]-o-oxazine (VIb), m.p. 103.5-104.5°. In later experiments, ethanol was used as solvent, and in these the adduct of bicyclohexenyl and nitrosobenzene was obtained with a yield of 43%, and the adduct of p-nitrosotoluene was obtained in a yield of 40%.

The adducts of nitrosobenzene with 2,3-dimethyl-1,3-butadiene and with 1-phenyl-1,3-butadiene were prepared in 1947 by Wichterle [3], but this author erroneously ascribed the structure denoted by 1,5-dimethyl-3-phenyl-6-oxa-2-azabicyclo [3.1.0] hexane to the addjuct formed with dimethylbutadiene, and the structure denoted by 1,5-diphenyl-6-oxa-2-azabicyclo [3.1.0] hexane to the adduct formed with phenylbutadiene.

EXPERIMENTAL

3,6-Dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine (Ia)

Nitrosobenzene (21.4 g = 0.2 mole), ether (300 ml), and 2,3-dimethyl-1,3-butadiene (16.4 g = 0.2 mole) were introduced into a flask, which was then placed in ice. After some time, pale-yellow needle-like crystals began to appear on the walls of the flask. After one day, the solution had acquired an orange color. The crystals were filtered off and washed with absolute ether. 4.6 g of substance was obtained. After recrystallization from ethanol, colorless glittering needles, m.p. 153-155° (dec.), were obtained.

Found %: C 74.01; 73.85; H 6.57; 6.60; N 9.07; 9.17

The ether was driven off from the filtrate, and the residue was vacuum-distilled. 3,6-Dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine (25.0 g, 66%) b.p. 125-126° at 3mm was obtained. After one recrystallization from ethanol, a colorless finely crystalline substance, m.p. 39.5-40.5° was obtained.

Found %: C 76.44; 76.22; H 8.16; 8.29; N 7.38; 7.27
$C_{12}H_{15}ON$. Calculated %: C 76.15; H 7.99; N 7.40

2,3-Dimethyl-4-phenylamino-2-buten-1-ol (II)

A solution of 3,6-dihydro-4,5-dimethyl-2-phenyl-1,2,2H-oxazine (18.9 g = 0.1 mole) in glacial acetic acid (200 ml) was introduced into a bottle, and zinc dust (20 g) was added. The bottle was closed with a stopper and shaken vigorously for 10 min; more zinc dust (20 g) was then added, and the bottle was shaken for a further 15 min. The reaction mixture was diluted with 200 ml of water, and caustic soda (200 g) was added. The resulting alkaline solution was steam-distilled to remove substances that were volatile in steam; 0.75 liter of distillate was collected. The solution remaining in the flask was filtered hot from the precipitate present. The filtrate was cooled and extracted 4 times with benzene (4×100 ml). The benzene extract was washed with water, the benzene was driven off, and the residue was fractionated under reduced pressure. The product was 2,3-dimethyl-4-phenylamino-2-buten-1-ol (15.7 g, 76%), with the following constants: b.p. 154.5-155° at 2 mm; d_4^{23} 1.0501; n_D^{20} 1.5744; found MR_D 66.12, calculated MR_D 66.60; EMR_D 1.54. The substance is an almost colorless very viscous liquid, which yellows on standing.

Found %: C 75.09; 75.07; H 9.29; 9.05; N 7.29; 7.35
$C_{12}H_{17}ON$. Calculated %: C 75.35; H 8.96; N 7.32

Diacetyl Derivative of 2,3-dimethyl-4-phenylamino-2-buten-1-ol

A solution of 2,3-dimethyl-4-phenylamino-2-buten-1-ol (8.35 g, 0.04 mole) was introduced into a flask fitted with a reflux condenser. The flask was heated on a [illegible] and acetic acid and excess acetic anhydride were then distilled off under reduced pressure. The residue was distilled. The diacetyl derivative of 2,3-dimethyl-4-phenylamino-2-buten-1-ol (10.0 g, 90% of theoretical) had the following constants: b.p. 157-158° at 1 mm; d_4^{20} 1.0774; n_D^{20} 1.5237; found MR 77.27; EMR$_D$ 0.87. It is a colorless, very viscous liquid.

Found %:	C 69.81, 70.01;	H 8.09, 8.07;	N 5.04, 5.23
$C_{16}H_{21}O_2N$. Calculated %:	C 69.79;	H 7.69;	N 5.09

3,6-Dihydro-4,5-dimethyl-2-(p-tolyl)-1,2,2H-oxazine (Ib)

p-Nitrosotoluene (18.16 g, 0.15 mole), 220 ml ether, and 2,3-dimethyl-1,3-butadiene (12.3 g) were introduced into a flask, which was placed in ice for one day. The ether was then driven off, and [illegible] was steam-distilled. A slightly yellowish crystalline substance came over in the distillate, and it was filtered and dried. 3,6-dihydro-4,5-dimethyl-2-(p-tolyl)-1,2,2H-oxazine (16.5 g, 54% of theoretical) was obtained (m.p. 62°). After one recrystallization from ethanol, colorless fine crystals, m.p. 62-63°, were obtained.

Found %:	C 76.90, 77.03;	H 8.64, 8.50;	N 7.08, 7.17
$C_{13}H_{17}ON$. Calculated %:	C 76.81;	H 8.43;	N 6.89

3,6-Dihydro-2,6 (or 2,3)-diphenyl-1,2,2H-oxazine (IVa or Va)

Expt. 1. A solution of nitrosobenzene (17.1 g, 0.16 mole) in 200 ml ethanol was cooled in ice, and [illegible] g of trans-1-phenyl-1,3-butadiene was added. After an hour, colorless needles began to separate, and the amount formed gradually increased. By the next day, the reaction solution had acquired a pale-yellow color. The crystalline substance was filtered off and washed with alcohol and ether. An adduct (30.4 g) of m.p. 82-83° was obtained. A further quantity (2.0 g) of the adduct was obtained from the mother liquor. Total yield 32.4 g (85% of theoretical). M.p. after one recrystallization from ethanol was 84.5-85°.

Found %:	C 81.22, 81.18;	H 6.46, 6.46;	N 5.98, 6.08
$C_{16}H_{15}ON$. Calculated %:	C 80.98;	H 6.37	N 5.90

Expt. 2. An ice-cooled solution of nitrosobenzene (6.5 g, 0.06 mole) in 45 ml pyridine was added to an ice-cooled solution of trans-1-phenyl-1,3-butadiene (7.9 g, 0.06 mole) in 45 ml pyridine. The flask was placed in ice overnight.* The pyridine was distilled off under reduced pressure. After two recrystallizations from ethanol, the adduct (7.9 g) was obtained in the form of yellowish needles, m.p. 82-83°, yield 55% of theoretical.

3,6-Dihydro-2-phenyl-6 (or 3)-(o-tolyl-1,2,2H-oxazine (IVb or Vb)

trans-1-Phenyl-1,3-butadiene (6.5 g, 0.05 mole) was added to an ice-cooled solution of o-nitrosotoluene (6.1 g, 0.05 mole) in 80 ml ethanol. The flask was placed in ice for one day. A considerable quantity of colorless needle-like crystals separated. The adduct was filtered off and washed with cold ethanol. The yield of adduct was 10.1 g (80% of theoretical). M.p. after recrystallization from a mixture of ethanol and light petroleum was 46-47°.

Found %:	C 81.52, 81.57;	H 6.94, 6.89;	N 5.66, 5.67
$C_{17}H_{17}ON$. Calculated %:	C 81.21;	H 6.84;	N 5.57

3,6-Dihydro-2-phenyl-6 (or 3)-(p-tolyl)-1,2,2H-oxazine (IVc or Vc)

An ice-cooled solution of trans-1-phenyl-1,3-butadiene (11.3 g, 0.09 mole) in 25 ml ethanol was added to an ice-cooled solution of p-nitrosotoluene (9.7 g, 0.08 mole) in 100 ml ethanol. The flask containing the reaction mixture was placed in ice for 2 days. A large quantity of colorless needle-like crystals separated, and the reaction solution became light-yellow. The crystals were filtered off and washed with cold alcohol. The yield of adduct was 16.1 g (80% of theoretical). M.p. after recrystallization from ethanol was 66-67°.

Found %:	C 81.37, 81.46;	H 6.96, 6.82;	N 5.86, 5.86
$C_{17}H_{17}ON$. Calculated %:	C 81.21;	H 6.84;	N 5.57

1,2,3,4,4a,6a,7,8,9,10-Decahydro-6-phenyl-6H-dibenz [c,e,]-o-oxazine (VIa)

Expt. 1. An ice-cooled solution of nitrosobenzene (10.7 g, 0.1 mole) in 50 ml pyridine was added over 30 minutes with shaker to an ice cooled solution of bicyclichexenyl (16.2 g, 0.1 mole) in 10 ml pyridine. The flask

*By the next day, the solution had become brown.

solution acquired an orange-red color after ... reduced pressure. The resinous residue partially crystallized on ... cold alcohol and ether. The yield of adduct, which was of ... g (39% of theoretical). After one recrystallization from ...

... H 8.74, 8.48; N 5.24, 5.29
... H 8.60; N 5.20

... ml ethanol, and nitrosobenzene (10.7 g, 0.1 mole) were introduced into a bottle, which was closed with a stopper and shaken mechanically at room temperature for 2 hours. The crystals that separated were filtered off and washed with cold alcohol (the solution had become orange). Yield of adduct ... g was separated from the mother liquor. Total yield was 11.5 g (43% of theoretical). M.p. after recrystallization from ethanol was 101-102°.

1,2,3,4,4a,5,6,7,8,12b-Decahydro-6-phenyl-6H-dibenz [c,e]-o-oxazine (VIb)

Expt. 1. An ethereal solution of p-nitrosotoluene (5.05 g, 0.05 mole) in 50 ml pyridine was added over 20 minutes with shaking to an ethereal solution of bicyclohexenyl (8.1 g, 0.05 mole) in 10 ml pyridine. The flask containing the reaction mixture was left overnight in ice. The solution became orange-red. The pyridine was driven off under reduced pressure. The resinous residue partly crystallized on standing. The crystalline substance was filtered off and washed with cold alcohol. The yield of adduct in the form of almost colorless crystals was 4.2 g (30%). After one crystallization from ethanol, colorless needles, m.p. 103.5-104.5°, were obtained.

Found %: C 80.80, 80.58; H 8.89; 8.99, 4.96, 4.88
$C_{19}H_{25}ON$. Calculated for C 80.50; H 8.86; 4.94

Expt. 2. Bicyclohexenyl (6.5 g, 0.04 mole), 60 ml ethanol, and p-nitrosotoluene (4.8 g, 0.04 mole) were introduced into a bottle, which was closed with a stopper and shaken mechanically at room temperature for 2 hours. The crystals that separated were filtered off and washed with cold alcohol. Yield of adduct: 4.3 g. A further amount (0.2 g) was isolated from the filtrate. Total yield was 4.5 g (40% of theoretical). After one recrystallization from ethanol, the adduct melted at 103.5-104.5°.

SUMMARY

1. A study has been made of the reactions of 2,3-dimethyl-1,3-butadiene, trans-1-phenyl-1,3-butadiene, and bi-1-cyclohexen-1-yl with aromatic nitroso compounds.

2. The following adducts have been prepared: 2,3-dimethyl-1,3-butadiene with nitrosobenzene and with p-nitrosotoluene; trans-1-phenyl-1,3-butadiene with nitrosobenzene, with o-nitrosotoluene, and with p-nitrosotoluene; bi-1-cyclohexen-1-yl with nitrosobenzene and with p-nitrosotoluene.

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* See Consultants Bureau translation, p. 339.

CURRENT EVENTS

SESSION OF THE DIVISION OF CHEMICAL SCIENCES DEVOTED TO THE 125TH ANNIVERSARY OF THE BIRTH OF N.N.BEKETOV

On January 26, 1952, at a joint session of the Division of Chemical Sciences of the USSR Academy of Sciences and the Committee on the History of Chemistry, a notable occasion was celebrated—the 125th anniversary of the birth of N.N.Beketov.

"The contribution made by Russian chemists to world science," said Corresponding Member A. F. Kapustinsky when opening the celebration session, "is indeed an invaluable one. Well-merited fame is associated with the names of Mendeleev, creator of the Periodic Law, Butlerov, creator of the theory of the structure of organic compounds, Zinin, pioneer in the chemistry of aniline compounds, Klaus, foremost chemist in the field of the platinum metals and discoverer of ruthenium, Hess, founder of thermochemistry, and the 'cohort of the famous', which include Markovnikov, Zaitsev, and other foremost workers in our native chemical science.

"In celebrating the 125th anniversary of the birth of one of the greatest chemists of this brilliant period in the history of chemistry—Academician Nikolay Nikolaevich Beketov, founder of modern physical chemistry and a remarkable scientist, whose numerous works, particularly those on thermochemistry, are deserving of the highest praise—we render that which is due to his services as a pioneer and as a continuator of the work of Lomonosov."

A paper on the life and activities of Academician N.N.Beketov was read by Ya.L.Turchenko, a candidate for the doctorate at the Institute of the History of Science. He gave a brief biography of N.N.Beketov, from which it was evident that Beketov was in close touch with such celebrities of chemistry as Zinin, Butlerov, and Mendeleev. Zinin's influence had its effect in the molding of Beketov as a scientist, while his association with Professor Ilyenkov, a notable educator, helped him to acquire aptitude as a teacher. Beketov's aim was to work in St.Petersburg with the celebrated chemist Zinin, but this could not be arranged. As there was no available post for him in St.Petersburg, he was compelled to take up duties as an assistant lecturer at Kharkov University, where he worked for 32 years. As he was a talented lecturer, he enjoyed great popularity, and his lectures drew large audiences.

Beketov took an interest in the training of specialists for his native land: he organized practical work and scientific investigations for his students and gave also a supplementary lecture course entitled "The Relations between Physical and Chemical Phenomena". With the object of furthering science and providing training for chemists, Beketov secured the establishment of a physicochemical department in Kharkov University, and in 1865, 21 years before such courses were introduced into the curriculum of Western universities, he began to deliver a course in physical chemistry—the first since that given by Lomonosov.

At an international congress of chemists held in the sixties of the last century, the fundamental concepts of Lomonosov on atoms and molecules were formulated anew. After the congress, Beketov wrote: "It is clear that he was concerned with questions about the structure of matter in general and about the molecular and atomic changes that occur in matter. The originality and clarity of his views on this subject are most impressive; he had arrived by reasoning at a concept that took its place in science only a century later. It is therefore easy to see why his contemporaries not only failed to understand him, but even treated his ideas in hostile fashion."

Beketov reacted actively and warmly to the discoveries of his brilliant compatriots. In his correspondence with A.M.Butlerov, he rejoices at the latter's successes: "I thank you most heartily," he wrote to Butlerov, "for sending me your 'Introduction to the Study of Organic Chemistry'. Your book could not be more opportune, in this present transitional period. All of those here who are concerned with chemistry think very highly of your book; they fell upon it with eagerness, particularly as your name, so closely associated with recent progress and new trends in science, endows it with special authority."

He welcomed Mendeleev's periodic law with enthusiasm. "Much work and the mind of a genius was required for the development of this exact system. Dmitri Ivanovich, through his great insight, was led to make alterations in certain atomic weights, and, finally, the periodic system that he had created showed him that certain gaps existed in the sequence of atomic weights, and, with the boldness of the man who really believes in the law that he has

discovered, he predicted the existence, and possibility of discovery, of the missing members of the series of elements... ....no law had hitherto existed in chemistry that would permit the prediction of the existence of this or that element of a particular atomic weight and having certain physicochemical properties. Such a law was discovered and developed in brilliant fashion by Dmitri Ivanovich."

In 1872, with Beketov's active participation, a society for experimental science was created at Kharkov University. Also, stated Turchenko, Beketov's scientific work was highly esteemed by Zaitsev and Butlerov, who presented Beketov for election as a corresponding member of the Academy of Sciences. In their presentation address, made on November 8, 1877, it is stated that "Beketov undoubtedly holds one of the most honored places among senior Russian chemists. He commenced his scientific activity in 1853 and has continued it with constant success up to the present time. The outstanding feature of Professor Beketov's work is its concern with fundamental general questions of chemistry, that is to say, with those questions whose solution has special importance for the science."

After the death of the senior Russian chemist Zinin, Butlerov put forward the names of Mendeleev and Beketov as candidates for the vacant chair of chemistry and technology. However, the reactionary governing body actively opposed this proposition and put forward the name of Beilstein. Right up to his death, Butlerov fought for the honor of Russian science and of Russian scientists.

Beketov's world-view was formed under the favorable influence of the ideas of the revolutionary democrats —the classics of Russian philosophical thought—and it determined his completely negative attitude to the tsarist regime. The following note occurs in his manuscripts: " .... Is it possible that the monarchy, the army, the war, the police, and finally ...(undecipherable)... the government, etc., are really necessary for the well-being of humanity ?" and the answer is given: "yes, they are as necessary as a bump on the forehead of a man who is falt(ering) in a space that is devoid of light."

Beketov characterized his attitude to socialists and communists in the following words: "When one knows in whose hands the fate of the people lies and how difficult it is under such conditions for the people to organize society for their own convenience and not for that of the government, it is impossible not to sympathize with every attempt to find sensible and acceptable (national) foundations for the social order. Everyone, of course, has heard of the socialists and communists, but everyone has also hastened to convince himself that these are local utopians without taking the trouble to become acquainted with these new tendencies."

Beketov's work in physical chemistry was discussed by Professor N.A.Izmail ov of Kharkov University. During the 60 years of his scientific activity — said Izmailov—Beketov witnessed the birth of a great many views in chemistry; some of them developed, others died. With very few exceptions, all Beketov's researches in physical chemistry were devoted to chemical affinity and to the way in which this affinity is determined by the properties of the elements. Beketov examined various aspects of the relation between structure and properties: 1) the thermodynamics of affinity, 2) the relation between the stability of compounds and the structure of the atoms, their volumes, and the changes in volume in the formation of the compounds, 3) the regularities to be observed in the heats of formation of compounds, 4) the energy of the elements and their structure. As a result of his examination of these properties, he established the exceptional reducing properties of aluminum.

In his doctorate thesis, the results of his investigations on the displacement of one element by another are brought together. In his physical chemistry course, he points out the limitations of Berthelot's principle, which does not permit a fall in temperature in a chemical process. Beketov asserted that "every chemical change occurring without the performance of external work proceeds only in the direction leading to the greatest evolution of heat, and every system tends to change into one that corresponds to the greatest evolution of heat." Beketov ended his analysis of Berthelot's principle with the words: "and for this reason, Berthelot's principle must, in any case, be regarded as incomplete and one-sided." Beketov introduced the concept of "decomposition pressure", which is close to the concept of "degree of dissociation"; he examined the conditions under which reactions proceed when one component is removed from the sphere of reaction; and he examined the effect of temperature on exothermic and endothermic reactions.

Beketov was not interested in the mere accumulation of facts; every experiment that he carried out was designed with the object of developing and confirming his views. He made a number of generalizations about heat effects. As an illustration of the great evolution of heat that occurs when compounds are formed with an accompanying high contraction in volume, he made a comparison of the heat changes and contractions occurring in the formation of chlorides, bromides, iodides, and oxides. Beketov established also the variability of the heat of reaction when one element is displaced by another, thus contradicting the assertions of certain chemists, who had declared it to be constant. He must be assigned priority for his treatment of heats of reaction, which he showed to follow an additive law.

Izmailov, in assessing Beketov's results from the point of view of modern concepts on atomic structure, the nature of the chemical bond, and bond strength, marveled at the insight of this scientist, who penetrated so deeply, on the basis of thermodynamic data, into the mechanism of the formation of compounds. On the basis of his theoretical researches, Beketov arrived at the correct explanation of the reducing effect of clays and developed the method of aluminothermy.

Having based his work on the relation between the chemical behavior of elements and their structures and properties, Beketov considered also the possibility of their undergoing change; he expressed the view, which is quite correct, that if atoms should be found to be divisible, then processes involving this divisibility would be quite different in character from chemical processes and would be accompanied by enormous changes in energy. He expressed this idea particularly clearly in his lectures on thermodynamics at Moscow University in 1890: "...we may suppose that elements were formed from matter that was still more dynamic than they are themselves and that they have retained some fraction of the energy that was evolved, probably in very large amount, in their formation."

Owing to his attitude toward the elements, he was prepared for the discovery of radioactivity, and took a great interest in it. In his article "The Energy of the Elements" he expressed completely correct views on the mechanism of radioactive changes, on the source of the energy in radioactive changes, and on the stability of the elements.

In conclusion, Izmailov said that Beketov's name had gone down in the history of science primarily as that of the founder of physical chemistry, one of the originators of the mass-action law, the founder of aluminothermy, the chemist who first opened up the question of the relation between the structure and the properties of the elements and solved it in his own way, and the chemist who correctly stated the question of changes in the elements and of the energy changes accompanying these processes.

Dear Comrade Editor,

In a number of my papers of the period 1940-1948, when I was concerned with the investigation of the properties and structures of addition products formed between metal salts and unsaturated compounds, I introduced the ideas, concepts, and language of the so-called "theory of resonance" in order to explain the complex chemical behavior of these compounds.

In recent years it has become more and more clear to me that the "theory of resonance and mesomerism" is idealistic, methodologically invalid, and of no use for investigation purposes.

I came forward with criticism of the "resonance theory" at a number of meetings, in particular at an open session of the Scientific Council of the Institute of Organic Chemistry of the USSR Academy of Sciences, at an open session of the Methodology Seminar of the Chemistry Faculty of the M.V.Lomonosov Moscow State University, and at other places. Later, together with seven other authors, I criticized the idealistic "theory of resonance" in the pages of "Progress in Chemistry", 1950.

I consider it to be my duty to announce in this letter that the concepts of superposition of structures, of ionic and covalent contributions to the state of bonds, and of the hybrid, resonance, or mesomeric structure of molecules, and certain other concepts, introduced into the literature mainly by Pauling and Ingold and, I regret to say, taken up in an uncritical fashion also by me, are unscientific and must be driven out of science.

It follows from what I have said that the explanations that I gave for the pecularities in chemical behavior of compounds such as:

$ClCH = CH - HGCl$[1], $(ClCH = CH)_2Hg$[1],

$ClCH = CHCl_2$[2], $O = C(N < C_5H_{10})(HgCl)$[3]

are erroneous (they amounted to the assumption of the existence of superimposed structures).

A critical examination of my own work has shown me that the matter of value contained therein is that which is based on A.M.Butlerov's theory – establishment of the structure of compounds of classes indicated above, development of methods for their synthesis, and investigation of their properties from the point of view of the manifestation of the mutual effects of atoms.

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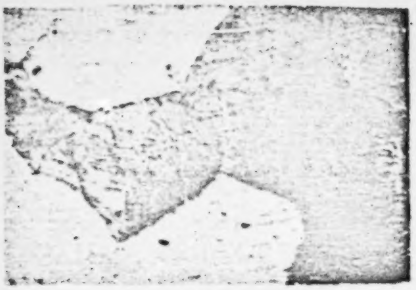
R. Kh. Freidlina

hanical Properties of Alloys of the
nesium – Cadmium System (page 383).



a

b

. 4. Microstructure of the alloy containing 50 atom-% Cd (X 100). a) Quenched; b) annealed.

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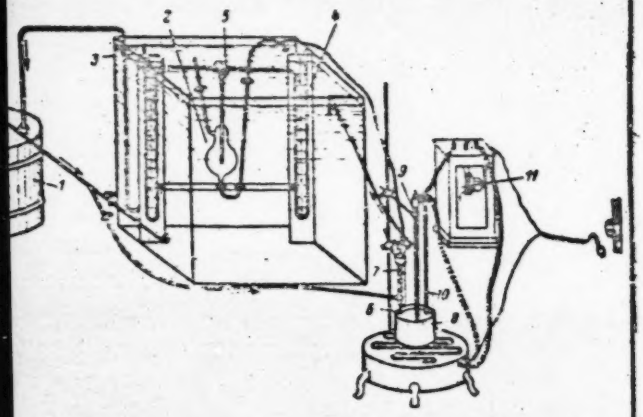

1. Diagram of apparatus: 1) thermostat; 2) thermostated el of the measuring system; 3) water manometer; 4) mercury ometer; 5) three-way tap for switching from one manometer c other; 6) tube for decomposition of acid; 7 thermostatic et of the reaction tube; 8) bath containing Wood's alloy; ontact thermometer for temperature regulation; 10) control nometer; 11) electromagnetic relay.

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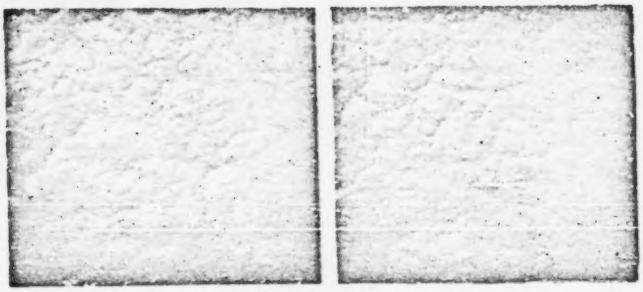
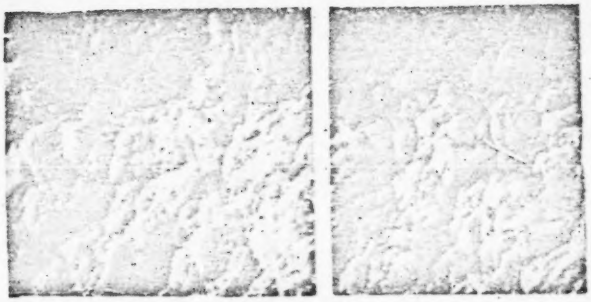


Fig. 2.



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